

**Workshop source term : from
characterization to prediction**

Rapport final

BRGM/RP-55500-FR
Avril 2007

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Workshop source term : from characterization to prediction

(Atelier terme source : de la caractérisation à la prédiction)

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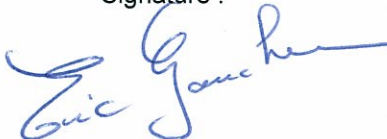
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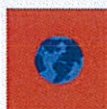
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Synthèse

Introduction

Un atelier ayant pour sujet « Terme source : de la caractérisation à la prédiction » a été organisé à Paris les 19 et 20 Octobre 2006 par l'ADEME et le BRGM. Les sujets proposés ont été déterminés en référence aux recommandations de l'Europe sur la gestion des déchets et en particulier à l'utilisation croissante d'essais et de modélisations destinées à prédire les impacts potentiels de différentes options de gestion (réutilisation, recyclage, stockage, etc.).

Les besoins

Pour répondre aux recommandations de l'Europe sur la diminution de la consommation des matières premières minérales, outre la réorganisation des procédés industriels, un recyclage de plus en plus poussé des sous produits devra être fait. Mais cette réutilisation devra encore être plus respectueuse de l'environnement et les règles d'utilisation plus contraignantes. Ainsi la politique européenne pour la mise en décharge et dans certains pays de l'union pour la valorisation, connaît ces dernières années une très forte impulsion vers l'évaluation physico-chimique et la prévision du comportement environnemental des déchets. Ceci s'est traduit concrètement par la mise en place, au niveau européen, de démarches normatives basées principalement sur la mise en oeuvre d'essais, notamment de lixiviation, destinés à renseigner sur l'émission de polluants par le déchet et aider à établir des modèles d'émission. Ces essais doivent aider à appréhender ce que l'on appelle le « terme source », c'est à dire le comportement à la lixiviation d'un déchet dans des conditions spécifiées (voir EN 12920).

Introduction

A workshop entitled "Source Term: from characterization to prediction" was held in Paris on October 19th and 20th, 2006 and organized by ADEME and BRGM. The proposed topics were determined with reference to European recommendations regarding waste management and in particular to the increased use of testing and modelling for predicting the potential impacts of different management options (reuse, recycling, landfilling, etc.).

The need

In response to European recommendations concerning the dwindling consumption of mineral raw materials, and also to the reorganization of industrial processes, there is a definite need for an increasingly thorough recycling of by-products. However, this reuse must be ever more respectful of the environment and conform to tight rules of application. European policy on waste disposal and, in certain EU countries, recycling, has thus generated over recent years a strong trend towards evaluating physico-chemical properties and predicting the environmental behaviour of waste. This has resulted in the commitment, at European level, to defining standards, based mainly on carrying out tests, particularly leaching tests, aimed at studying pollutant emission by waste and used to construct emission models. These tests must help us grasp the "source term", i.e. the behaviour of a given waste during leaching under specified conditions (see EN 12920).

Thèmes abordés

Ce séminaire se proposait de faire un point sur l'état des connaissances concernant le «terme source». Les différents thèmes abordés ont été les suivants (liste non exhaustive) :

- Réalisation des essais de lixiviation en laboratoire : quelles limites ? Quelles perspectives d'amélioration ?
- Extrapolation des essais en laboratoire à d'autres scénarios de percolation : possibilités et limites ?
- Modèles couplés transfert-chimie appliqués au terme source : outils d'aide à la compréhension du comportement et/ou outils de prédiction ?
- Saturation / non saturation : influence sur les équilibres géochimiques et sur le terme source ?
- Outils et bases de données conçus pour aider à l'interprétation des résultats analytiques.

Considered topics

This workshop was intended to gather experimenters and modellers to discuss the current state of knowledge concerning the "source term". The various covered included, but were not be restricted to:

- Undertaking leaching tests in the laboratory: what are the limits? What are the prospects for improvement?
- Extrapolation of laboratory tests to other percolation scenarios: what are the possibilities and limitations?
- Coupled chemistry-transfer models applied to the source term: tools that can help us better understand behavioural patterns and/or give more accurate predictions?
- Saturated / unsaturated conditions: what are the effects on geochemical speciation and source term behaviour?
- Tools and data bases designed to accompany the interpretation of the analytical results.

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1. Introduction (Introduction)

In order to abide by the recommendations from Europe on the reduced use of mineral raw materials and aimed at implementing a European society of recycling, in addition to the reorganization of industrial processes, it will be necessary to more thoroughly recycle industrial by-products: residues from industrial processes (manufactured residues, residues from energy production or from waste treatment), waste from transport networks (roads, rivers and canals, railways, seaports) or from the extraction of natural resources (mines, quarries). But this reuse will have to be ever more respectful of the environment and the rules of utilization will be more and more restrictive. This is why over the past number of years waste management policy has received strong impetus towards assessing and forecasting the physicochemical fate of waste.

In practical terms this has resulted in the drafting at the European level of legislation regulating the landfilling of waste (Directive 1999/31/CE and Decision 2003/33/CE) which was accompanied by standardisation efforts (acid-base neutralisation capacity measures, leaching at controlled pH, batch leaching, dynamic leaching by upward percolation, monolith leaching tests) that can provide characterization data some of which may serve to develop models that reproduce and predict behaviour. This is underlined by recent scientific publications that show an increasing usage of geochemical and hydrodynamic models.

Pour répondre aux recommandations de l'Europe sur la diminution de la consommation des matières premières Pour répondre aux recommandations de l'Europe sur la diminution de la consommation des matières premières minérales visant notamment à créer une société européenne du recyclage, outre la réorganisation des procédés industriels, une valorisation (réemploi, réutilisation, recyclage) de plus en plus poussée des différents types de résidus et sous produits devra être fait : résidus de procédés industriels (manufacturiers, de production d'énergie ou de traitement de déchets), des déchets d'entretien des infrastructures de circulation (routes, voies d'eau, rail, port) ou d'exploitation de ressources naturelles (mines et carrières). Mais cette valorisation devra être de plus en plus respectueuse de l'environnement et les règles d'usages seront de plus en plus contraignantes. Ainsi la politique de gestion des déchets connaît ces dernières années une très forte impulsion vers l'évaluation et la prévision de leur devenir physicochimique.

Ceci s'est traduit concrètement au niveau européen dans le cadre de l'élaboration des textes réglementant la mise en décharge (Directive 199/31/CE et Décision 2003/33/CE) qui s'est accompagné de la mise en place de démarches normatives (mesures de capacités de neutralisation acido-basiques, lixiviation à pH contrôlé, lixiviation en batch, lixiviation en percolation ascendante, essais de lixiviation sur monolithe,...) susceptibles de fournir des données de caractérisation, certaines pouvant servir à l'établissement des modèles de compréhension ou de prédiction. Sur cet aspect, l'examen des publications scientifiques récentes montre une utilisation de plus en plus fréquente des codes de calcul géochimique et hydrodynamique.

But the conclusions that can be drawn from these efforts are very lukewarm, due to the difficulty of having, at a European level, a coordinated or at least coherent management of the various data generated, other than simply the general methodology of leaching behaviour assessment (i.e. standard EN 12920).

Critical analysis of the different initiatives taken to date, both at French and European levels, suggest a certain lack of maturity in approaches that have come up against various hurdles:

- (a) The weakness of the approaches developed for the interpretation of measurements derived from leaching tests, with the consequence that information on possible usage is lacking.
- b) A lack of knowledge concerning the intrinsic nature of materials, minerals, speciation of the polluting elements, possible processes controlling the transformation of materials.
- (c) An oftentimes questionable use of hydro/geochemical numerical models.
- (d) Modelling codes that are ill suited for a coupled approach including thermodynamic, kinetic and hydrodynamic aspects of source term and transfers approach, which implies a decoupling that leads to unrealistic calculations.
- (e) A rather general absence of thermodynamic data relating to waste and amorphous phases.
- (f) The absence of a thermodynamic formalism adapted to chemical equilibrium in the non-saturated zone.
- (g) The extreme scarcity of synthesised data on the returns from waste management trials such as storage, implementation, and which include a description of the initial state of the system considered.

Mais, les constats que l'on peut faire autour de ces mises en œuvre sont très mitigés en raison de la difficulté d'avoir, au niveau européen, un cadre cohérent permettant une exploitation coordonnée ou du moins cohérente des différentes données issues des démarches proposées; outre celui méthodologique plus large de l'évaluation du comportement à la lixiviation en scénario (norme EN 12920).

En effet, l'analyse critique des différentes actions menées à ce jour, aussi bien au niveau européen que français, suggèrent une certaine immaturité des démarches qui se heurtent à différentes pierres d'achoppement :

- (a) La faiblesse des démarches de fond faites autour de l'interprétation des mesures issues des essais de lixiviation ayant pour corollaire l'absence d'indication sur le domaine d'utilisation possible, en particulier les limites.
- (b) Une méconnaissance de la nature intrinsèque des matériaux, des minéraux, de la spéciation des éléments polluants, des processus potentiels contrôlant la transformation des matériaux.
- (c) Une utilisation souvent critiquable des codes de calcul hydrogéochimique.
- (d) Des codes de calcul mal adaptés à une approche couplée, incluant la thermodynamique, la cinétique et l'hydrodynamique du terme source et des transferts, ce qui implique un découplage qui est nuisible au réalisme des modélisations.
- (e) Une absence assez générale de données thermodynamiques applicables aux déchets et aux phases amorphes.
- (f) L'absence de formalisme thermodynamique pour l'approche des équilibres en zone non saturée.
- (g) L'extrême rareté de données synthétisées sur des retours d'expériences sur la gestion des déchets tels que stockage, mise en œuvre, et qui incluent la caractérisation de l'état initial du système considéré.

These elements show that many efforts need to be made in France as in Europe in order to, on the one hand, develop a common expertise around leaching and related modelling of waste behaviour in percolation scenarios and environmental impacts and, on the other hand, identify the deadlocks and scientific levers.

In conclusion it was urgent to gather the main French and European specialists around this set of themes, in order to provide a current state-of-the-art and to generate useful exchanges for preparing future collaborations.

Ces constats montrent que de nombreux efforts doivent encore être faits en France comme en Europe pour d'une part, développer une expertise commune autour de la lixiviation et les modélisations connexes que l'on peut faire concernant le comportement des déchets en scénario et leurs impacts sur l'environnement, et d'autre part, identifier les verrous et les leviers en particulier scientifiques.

En conclusion il devenait indispensable de rassembler les principaux spécialistes Français et Européen autour de cette thématique pour faire un point des connaissances et provoquer des échanges fructueux pour préparer le terrain de futures collaborations.

2. Atelier (Workshop)

2.1. ATTENDANCE

The meeting gathered 34 participants coming from several European countries and also two participants from the USA (Table 1). During the two days, 16 oral presentations covered all the program topics and two round tables were organized respectively on: i) Which are the essential steps required in order to characterise a waste? ii) From characterization to environmental assessment, where are the knowledge gaps and the needs?

The workshop was concluded by a summary and prospect session managed by David Kosson from Vanderbilt University.

2.2. PROGRAM

The subjects developed during this workshop can be classified according to three broad topics:

- i) Characterisation of waste at different scales
- ii) Geochemical modelling
- iii) Coupled modelling
- iv) Experience feedback

A table illustrating the workshop content is given below (Table 2).

2.1 PARTICIPATION

La réunion a rassemblé 34 personnes venant de plusieurs pays Européens et deux personnes des Etats-Unis (Tableau 1). Pendant deux jours, 16 interventions orales ont couvert les différents sujets du programme et deux tables rondes ont été organisées autour des questions suivantes : i) Quelles sont les étapes essentielles de la caractérisation d'un déchet ? ii) De la caractérisation à l'évaluation environnementale quelles sont les pierres d'achoppement et les besoins ?

L'atelier a été conclu par une session de synthèse et de prospective animée par David Kosson de l'Université de Vanderbilt.

2.2 PROGRAMME

Les sujets développés pendant ce workshop peuvent être classés selon trois grandes thématiques :

- i) Caractérisation des déchets à différentes échelles
- ii) Modélisation géochimique
- iii) Modélisation couplée
- iv) Retours d'expériences

Un tableau illustrant le contenu de l'atelier est donné ci-dessous (Tableau 2).

Workshop source term
Atelier terme source

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Table 1 – List of the workshop participants (registered)
Tableau 1 - Liste des participants à l'atelier (inscrits)

19/10/2006	01:00	00:30	01:30		
	9:00	1	9:30	van der Sloot Hans	Characterisation leaching tests and geochemical modelling to define a source term for assessment of environmental impact
	9:30	2	10:00	Ute Kalbe	Validation of leaching test: a key issue towards reliable use of results
	10:00	3	10:30	Bottero Jean Yves et Rose Jérôme	Re-use of waste and behaviour of heavy metals : a molecular approach of the transfer mechanisms
	10:30	Coffee break	11:00		
	11:00	4	11:30	Rob N.J. Comans, Joris J. Dijkstra, Andre van Zomeren & Hans Meeussen	Characterisation and modelling geochemical processes controlling the leaching of contaminated materials: a generic approach applied to MSWI bottom ash
	11:30	5	12:00	Barna Ligia	pH dependence test interpretation throughout mineral dissolution/precipitation processes
	12:00	Meal	13:30		
	14:00	6	14:30	Johnson Annette	How uncertain can geochemical and hydrological information be for the long-term prediction of leachability
	14:30	7	15:00	Kosson David	Source-term conceptual models and challenges in predicting long-term performance of cement stabilized waste forms
	15:00	8	15:30	Vanderlee Jan	Present state and perspectives of reactive transport modelling for risk assessment
	15:30	9	16:00	Wahlstrom Margareta	Models for impact evaluation on landfill – aspects for proper modelling
	16:00	10	16:30	Lassin Arnault	Thermodem: a thermodynamic data base devoted to solid waste.
	16:30	Coffee break	17:00		
	17:00		18:30	Round table Chairing: Nzihou Ange	What are the essential steps to characterise a waste?
20/10/2006		00:30	01:30	01:00	
	9:00	11	9:30	de Windt Laurent	Coupled modelling of leaching tests and environmental processes applied to stabilized and MSWI wastes.
	9:30	12	10:00	Astrup Thomas	Prediction of Cr leaching from waste incineration residues
	10:00	13	10:30	Meeussen Hans (presented by H. Van der Sloot)	Predicting leaching of substances from porous materials with a reactive transport model (with references to ORCHESTRA)
	10:30	Coffee break	11:00		
	11:00	14	11:30	Hjelmar Ole	Leaching of contaminants from MSWI bottom ash used as sub-base in road construction: Results from a pilot scale test site
	11:30	Meal	12:30		
	12:30	15	13:00	Mehu Jacques	Pilot scale data input in understanding and prediction of leaching behaviour of utilisation of waste in civil engineering
	13:00	16	13:30	Dominique Guyonnet	A multiple-scale study of pollutant emission from MSW fluidized bed incinerator ash.
	13:30		15:00	Round table Chairing: Stegmann Julia	From the characterization to the environmental assessment where are the hurdles, the needs?
	15:00		15:30	Chairing: Kosson David	Summary and prospects
	15:30	Coffee break	16:00		End of the workshop

Table 2 – Program of the workshop

Tableau 2 – Programme de l'atelier

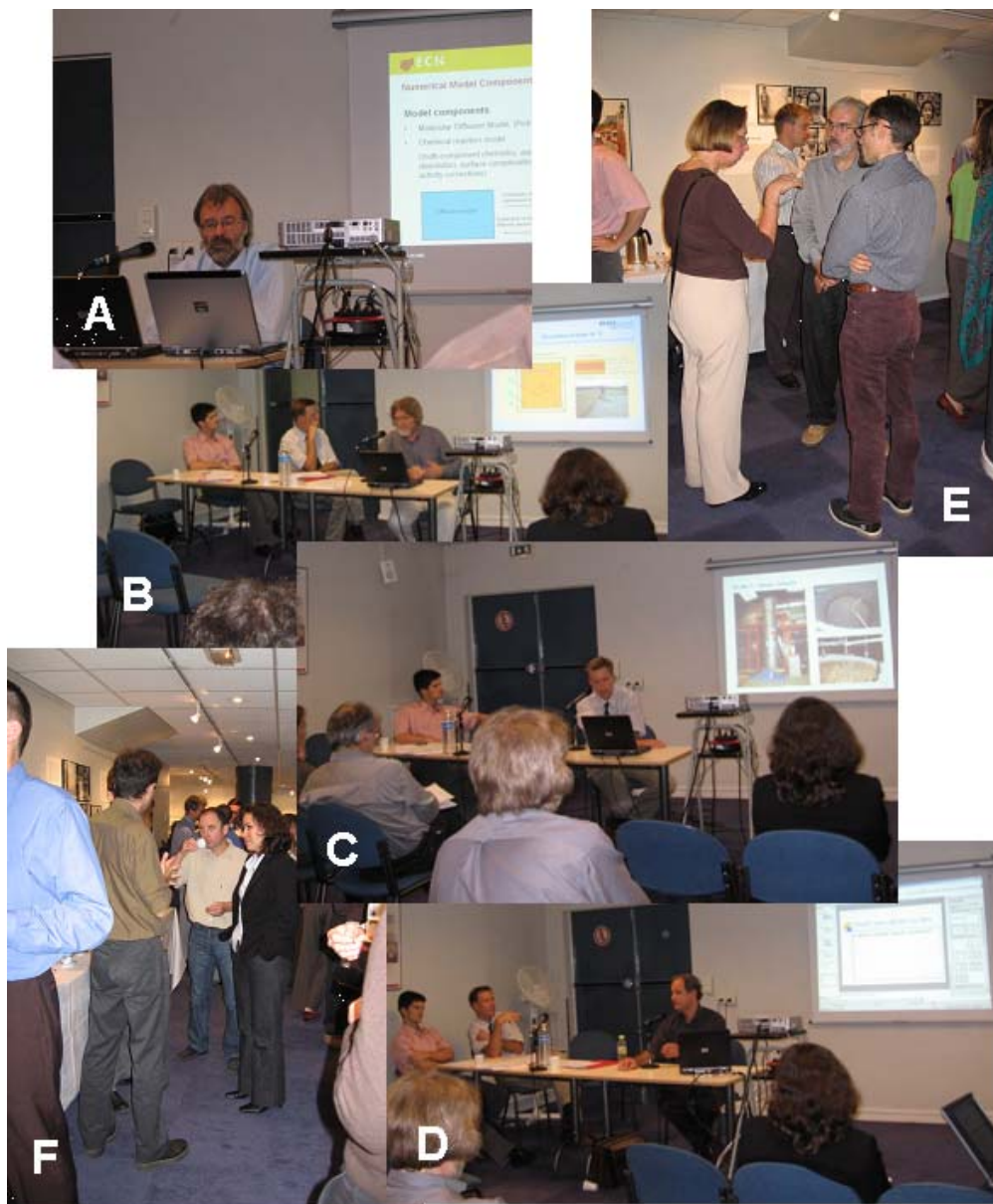


Figure 1 - Multiple photo-frame of the Workshop Source Term (Chairing : Dominique Guyonnet and Laurent Chateau); A) Hans van der Sloot presented the opening session; B) presentation by Ole Elmar; C) presentation by Dominique Guyonnet; D) synthesis and conclusions by D. Kosson; F and G the coffee breaks were opportunities of intense discussions between participants; F) Denis François (back) Rabbia Baddredine and Arnault Lassin, G) Margareta Walström, Jacques Méhu and Jerome Rose.

Photo 1 - Pêle-mêle de l'Atelier Terme Source (Présidence : Dominique Guyonnet et Laurent Chateau) ; A) Hans van der Sloot pour la session d'ouverture ; B) présentation de Ole Elmar et C) présentation de Dominique Guyonnet ; D) D. Kosson lors de la session de synthèse et conclusion ; F) et G), les pauses café ont été l'occasion d'intenses discussions entre les participants ; F) Denis François (de dos), Rabbia Baddredine et Arnault Lassin ; G) Margareta Walström, Jacques Méhu et Jérôme Rose

3. Tables rondes (Round tables)

In order to complete the traditional series of questions/answers at the end of each presentation, additional time was devoted to exchanges between participants during two round tables.

The first round table, chaired by Ange Nzihou, Professor at the Albi School of Mines, was focused on the characterisation of waste in terms of methodology and content in order to obtain the necessary information prior to assessing a percolation scenario according to standard EN 12920.

The second round table, chaired by Julia Stegeman, Doctor of Imperial College London, was aimed at exchanging on issues related to predictive modelling: what is the current state-of-the-art? What are the obstacles and levers identified in order to improve the quality of results and the "confidence" that end-users can have in decision that are derived from such calculations?

The main topics of discussion or of interest that emerged from the debates are listed below:

Afin de compléter les traditionnelles séances de question/réponses en fin d'intervention, une large place a été accordée aux échanges et aux débats par l'intermédiaire de deux tables rondes.

La première, animée par Ange Nzihou, Professeur à l'Ecole des Mines d'Albi, a été axée sur la caractérisation des déchets en termes de contenu et de méthode afin d'acquérir les informations nécessaires et suffisantes à une évaluation en scénario, notamment dans le cadre de la norme EN 12920.

La seconde, animée par Julia Stegeman, Docteur à l'Imperial College de Londres a permis d'échanger sur les aspects liés à la modélisation prédictive : quel est l'état des connaissances et des pratiques ? Quels sont les verrous et les leviers identifiés ou probables pour améliorer la qualité des résultats et la « confiance » des utilisateurs finaux dans le processus de prise de décision en découlant.

Les principaux sujets de discussion ou d'intérêt évoqués par les participants sont listés ci-dessous :

3.1. FIRST ROUND TABLE.

The questions proposed for the discussion by A. Nzihou were the following:

- o Are the existing tests (mainly leaching tests) necessary and sufficient for understanding the behaviour of a given waste?
- o What is the best approach (from the lab to the field or the opposite)?
- o How should exposure be taken into account (characterization, modelling)?
- o How can laboratory data be extrapolated in order to simulate field conditions?

From the discussions it follows that there is a need to improve characterisation and models in order to take into account:

- o kinetic effects,
- o redox phenomena (intrinsic potential and factors of influence),
- o contact times versus residence times,

3.1. PREMIERE TABLE RONDE

Les questions proposées à la discussion par A. Nzihou étaient les suivantes :

- o Est-ce que les essais existants (de lixiviation principalement) sont nécessaires et suffisants pour la compréhension du comportement d'un déchet ?

- o Quelle est la meilleure approche (du laboratoire au terrain ou l'inverse) ?

- o Comment prendre en compte (caractérisation, modélisation) les conditions d'exposition ? Lesquelles ?

- o Comment extrapoler les données de laboratoire pour simuler la situation de terrain ?

Des discussions il ressort qu'il convient d'améliorer la caractérisation et la modélisation afin de mieux prendre en compte :

- o des phénomènes cinétiques,
- o des phénomènes rédox (potentiel intrinsèque et facteur d'influence),
- o du temps de contact/ temps de séjour,

- o physical properties (total porosity, accessibility, pore distributions, reactive solid distribution),
- o exposure conditions (carbonation, redox – cf. supra – intermittence of water regime, etc.),
- o interaction between chemical and physical evolutions of the solid.

Knowledge of the characteristics of the waste as well as of the influencing factors are essential for realistic modelling. But two aspects appear as particularly critical:

- o The definition of boundary conditions,
- o Feedback from field experiments

Another challenge is related to the notion of equilibrium. Progress must be made with respect to the present situation where:

- o The models assume chemical equilibrium while in reality the reactions are not at equilibrium,
- o Tests are performed in situations of pseudo-equilibrium that are different from field conditions.

3.2. SECOND ROUND TABLE

The discussions of the second round table pertained to issues that are summarized below.

- o Do we understand the geochemistry of waste as well as we need to for environmental assessment?
 - How important are kinetic effects on surface/pore water interaction, etc?
 - Are our standard tests adequate?
 - Other gaps?
- o How can we make a link between our understanding of the source term and actual behaviour in field?
 - Are there important gaps in our quantitative understanding of mechanisms?

- o des propriétés physiques (porosité totale, accessible, distribution poreuse, quantité de solide réactif),
- o des conditions d'expositions (carbonatation, redox – cf. supra – intermittence de l'exposition à l'eau, etc.),
- o interactions entre évolutions chimiques et physiques du solide.

La connaissance des caractéristiques du déchet ainsi que des facteurs déterminants apparaît essentiel pour modéliser. Cela étant, deux points apparaissent comme liés et critiques :

- o La définition des conditions aux limites,
- o Le retour d'expérience du terrain.

Un autre challenge apparaît en ce qui concerne la notion d'équilibre. Il consiste à dépasser la situation actuelle qui est la suivante :

- o Les modèles supposent l'équilibre chimique alors qu'en réalité les réactions ne sont pas à l'équilibre,
- o Les essais sont menés dans des conditions de pseudo-équilibre différentes de celles régnant sur le terrain.

3.2 SECONDE TABLE RONDE

Les discussions de la seconde table ronde ont eu trait à des aspects qui sont regroupés ci-dessous :

- o Est-ce que nous comprenons suffisamment la géochimie des déchets pour réaliser des évaluations environnementales ?
 - Quelle est l'importance des effets cinétiques sur les interactions entre surfaces et eau porale, etc. ?
 - Est-ce que nos essais normalisés sont adéquats ?
 - Autres lacunes ?
- o Comment établir le lien entre notre compréhension du terme source et les phénomènes observés sur le terrain ?
 - Y'a-t-il d'importantes lacunes de compréhension des mécanismes?

- How can we validate models? With which scenarios? With which data? Others?
- Is the final level of uncertainty small enough to make quantitative/qualitative predictions? Over what scales of time and space?
- How far can we extrapolate from validated scenarios?

With respect to model “validation”, it is important to distinguish between model verification (its ability to reproduce laboratory data) and true validation, which can only be performed if the verification step has been completed and which involves testing the predictive capacity of the model in terms of scale or temporal changes.

Participants also recognize the importance of communication towards decision-makers and the scientific community. This entails complementary studies that address the following aspects:

- o Provide working hypotheses and limitations (indicating in particular what are the fitting parameters),
- o Explicitly clearly the objectives of the modelling: orders of magnitude, trends, precise predictions, other,
- o Characterise uncertainties and the domain of validity of the results,
- o Develop guides of best practice for the use of models in this field and for thermodynamic databases,
- o Vocabulary: validation / vérification (cf. supra).

Field experiments are essential in order to address true exposure conditions (source heterogeneity, flow regime, boundary conditions, etc.) and to validate the models because they are performed at a scale that is much larger than laboratory experiments and over periods of time that are generally much larger.

- Comment valider les modèles ? Avec quels scénarios ? Avec quelles données ? Autres ?
- Est-ce que le niveau d'incertitude suffisamment faible pour permettre des prédictions quantitatives/qualitatives ? Sur quelles échelles de temps et d'espace ?
- Dans quelle mesure peut-on extrapoler des scénarios validés ?

En ce qui concerne la “validation” de la modélisation, il y a lieu de faire une distinction entre la vérification du fonctionnement du modèle (capacité à reproduire des résultats au laboratoire) de la validation à proprement parler qui ne peut être réalisée que si la vérification est positive et qui consiste à tester la capacité prédictive du modèle en termes de changement d'échelle ou de temps.

Les participants s'accordent également à reconnaître l'importance de la communication, vers les décideurs et la communauté scientifique. Cela passe d'abord par des travaux complémentaires aux études de modélisation courantes, en s'attachant à couvrir les points suivants :

- o Fournir les hypothèses de calcul et les limites (en indiquant notamment quels sont les paramètres de calage),
- o Préciser ce que vise la modélisation : ordre de grandeur, tendance, simulation fidèle, autre,
- o Caractériser les incertitudes et le domaine de validité des résultats,
- o Elaborer des guides de bonnes pratiques / bonne conduite sur l'usage des modèles et des bases de données thermodynamiques,
- o Vocabulaire : validation / vérification (cf. supra).

Les expérimentations de terrain sont essentielles à la connaissance des conditions d'exposition (hétérogénéité de la source, conditions d'écoulement, conditions aux limites, etc.) et à la validation de la modélisation car elles sont réalisées à une échelle bien supérieure aux expérimentations de laboratoire et sur des durées qui sont généralement beaucoup plus longues.

4. Conclusions d'après les notes de D. Kosson (Conclusion from the D. Kosson's key notes)

Des différentes interventions et discussions sont ressorties un certain nombre de réflexions qui sont rassemblées dans cette conclusion. Le premier enseignement, qui vaut pour toutes les études présentées et qui doit être clairement souligné est que contrairement aux Sciences de la Terre, pour lesquelles la connaissance repose sur un passé de plus de 300 ans, les Sciences dites Environnementales en sont encore à leurs débuts. En raison de la complexité des phénomènes en jeu, il reste à parcourir un important chemin avant de parvenir à une véritable maîtrise de ces phénomènes et pouvoir prétendre à une véritable capacité prédictive en termes de risques.

4.1 L'EVALUATION DE LA LIXIVIATION : UN OUTIL INTEGRATEUR

Les évaluations du comportement à la lixiviation de matériaux de type « déchets » peuvent être considérées comme des approches intégratrices de la phénoménologie impliquée dans les interactions solide-liquide. Bien que les essais en laboratoire permettent d'identifier les processus spécifiques et de quantifier des paramètres intrinsèques liés aux matériaux, ils ne reproduisent jamais fidèlement les conditions réelles de terrain. Il est par conséquent nécessaire de clarifier les processus et les conditions de lixiviation au travers d'une démarche itérative faisant un aller-retour entre les études en laboratoire et les études de terrain. Pour une évaluation donnée, des scénarios de percolation doivent être définis qui constituent des simplifications acceptables des conditions spécifiques de terrain. Dans ce contexte, la modélisation est une étape incontournable permettant de traduire les résultats des essais en laboratoire en des données utilisables pour la simulation des scénarios.

To conclude, thoughts developed through various discussions and exchanges are summarised below. The main thought, which is valid for all studies presented deals with the difference in time scale between development of Earth science knowledge and of development of Environmental science knowledge: the first one has been developed through the last 300 years while the second one has been developed only recently. Due to the complexity of phenomenon involved in Environmental science, there is still a long way to come before achieving a real understanding of these phenomena and before being able to achieve predictive risk assessment.

4.1. LEACHING BEHAVIOUR ASSESSMENT: AN INTEGRATING TOOL

Assessing the leaching behaviour of waste-type materials can be considered as an integrating approach of the phenomena involved in liquid-solid interactions. While laboratory tests provide valuable information regarding specific processes and enable one to quantify material intrinsic parameters, they never accurately reproduce field conditions. It is therefore necessary to clarify the processes through an iterative procedure involving laboratory and field testing. For a given assessment, percolation scenarios must be defined which constitute acceptable simplifications of specific field conditions. In this context, modelling is a compulsory step that allows laboratory tests to be used to generate data values that are relevant for scenario simulation.

La modélisation est d'autant plus nécessaire que la complexité des conditions de terrain nécessite généralement l'utilisation d'outils de calcul performants adaptés à cette complexité. Cette dernière découle notamment de la présence de gradients spatiaux qui peuvent varier en fonction du temps, à la faveur d'événements épisodiques (par exemple en fonction de la pluie). Pour l'application des modèles de simulation, une définition adaptée des conditions aux limites est indispensable, de même qu'une bonne compréhension du comportement des polluants. Cette compréhension nécessite d'appréhender l'interaction entre de nombreux éléments (cations, anions, carbone organique dissous, etc.) pour différentes conditions géochimiques (pH, force ionique, potentiel rédox). Il faut tenir compte notamment des comportements différents des polluants en conditions saturées et non-saturées, de cinétiques de réactions aux interfaces entre les phases solides, liquides et gazeuses ainsi que de l'évolution physico-chimique (voire mécanique), de la matrice solide du déchet.

4.2 DES DECISIONS DE GESTION BASEES SUR UNE CONNAISSANCE SCIENTIFIQUE

La compréhension scientifique des phénomènes doit servir de base pour la prise de décision concernant la gestion des sources de pollution. Ainsi, la recherche définit les processus clés, les modèles conceptuels et un cadre réaliste pour les simulations. Mais l'utilisation des résultats de la recherche en vue de prises de décisions dans un cadre opérationnel nécessite une étape de simplification. Cette étape implique que la recherche doit fournir les données permettant d'identifier les processus déterminants, elle doit être en mesure de standardiser la collecte de données, les essais de caractérisation, la modélisation des scénarios et clarifier la démarche d'aide à la décision. Les incertitudes inhérentes aux différentes étapes doivent être identifiées ; fiabilité et précision des essais en laboratoire, fiabilité des modèles, etc. A cette fin, les comparaisons inter-laboratoires, ainsi que le bench-marking des modèles s'avèrent des outils précieux.

Modelling is particularly necessary considering the complexity of field conditions which requires the use of elaborate calculation tools that are adapted to this complexity. This complexity arises for example from the presence of spatial gradients that may vary as a function of time (for instance under the influence of rainfall episodes). For the use of simulation models, an adequate definition of boundary conditions is required, as well as a good understanding of pollutant behaviour. In order to reach such understanding it is necessary to address the interaction between the numerous elements involved (cations, anions, dissolved organic carbon, etc.) for different geochemical conditions (pH, ionic strength, redox potential). It is important to account for pollutant behaviour in saturated and unsaturated conditions, kinetic reaction rates at the interface between aqueous, solid and gaseous phases, as well as the physico-chemical (and mechanical) evolution of the solid waste matrix.

4.2. SCIENTIFIC UNDERSTANDING AS A BASIS FOR MANAGEMENT DECISIONS

The scientific understanding of phenomena must serve as a basis for taking decisions regarding management of the pollution sources. Thus research defines the key processes, the conceptual models and a realistic framework for simulations. But the use of research results for decision-making in an operational context requires a simplification step. This step implies that research must provide the data allowing the identification of key processes, it must be capable of standardizing data collection, characterization testing procedures, scenario modelling schemes and clarifying the decision-making process. Inherent uncertainties at the different stages must be identified; accuracy and precision of laboratory tests, model reliability, etc. For this purpose, inter-laboratory round robin assays and model benchmarking are useful procedures.

4.3 LES BESOINS LES PLUS CRITIQUES

Un premier besoin est la nécessité d'avoir des points de repères par rapport au milieu naturel pour caler les modèles. Il faut avoir la possibilité de faire des comparaisons, toutes proportions gardées, entre les données du laboratoire et du terrain pour des systèmes proches à homologues¹. Ces comparaisons faites à travers des descriptions de systèmes avant et après évolution, en prenant en compte les bilans hydriques et chimiques, doivent permettre d'améliorer la capacité prévisionnelle des modèles.

Un deuxième besoin comme décrit plus haut est de pouvoir proposer des démarches standardisées pour la mise en œuvre des essais, de la modélisation des scénarios, de la prise de décision, pour le contrôle qualité, etc.

Un troisième besoin critique est la nécessité de disposer de données fondamentales, caractéristiques des mécanismes clés influençant le comportement du terme source :

- Les constantes thermodynamiques pour les minéraux clés et ceci pour des conditions représentatives,
- Les paramètres cinétiques (par exemple la vitesse de carbonatation et son importance en fonction des matériaux et des conditions chimiques), les changements de phase pour les réactions clés et ceci pour des minéraux et des processus n'atteignant jamais l'équilibre (par exemple pour le cas des précurseurs minéraux colloïdaux).
- Le comportement des phases et l'impact de conditions d'humidité variables (courbes de rétention de l'eau, gaz et liquides, diffusivité, activité de l'eau,...).

¹ Homologue : système anthropique tel un ancien site de décharge historique permettant de faire des mesures et des observations.

4.3. THE MOST CRITICAL NEEDS

A first critical need is the need to have reliable field data in order to calibrate the models. It is necessary to be able to compare laboratory data to field data for natural systems that are similar or homologous². Such comparisons performed on systems observed before and after their evolution, taking into account water and chemical balances should help improve the predictive capability of models.

A second need is to provide standardized procedures for the implementation of tests, the modelling of scenarios and for quality control, etc.

Also needed are data that are characteristic of mechanisms that influence source term behaviour:

- Thermodynamic constants for key mineral phases at relevant conditions,
- Kinetic parameters for key reactions (for example carbonation rates and its extent as a function of material type and chemical conditions), phase changes for key reactions and for processes that never reach equilibrium (for example for the case of colloidal mineral precursors).
- Behaviour of mineral phases and impacts of variable moisture conditions (water retention curves, gas and liquid phase diffusivity, water activity).

² Homologous: anthropogenic system such as for example an old landfill site that provides opportunities for observations.

- L'évolution physique et chimique des matériaux originels.
- Des « courbes type » de comportement à la lixiviation dynamique, caractéristiques de classes de matériaux.

4.4 SUR QUELS ASPECTS CONCENTRER LES EFFORTS ?

Sur ce point, la réflexion reste ouverte. Il ne fait pas de doute que les ciments, les mâchefers d'incinération d'ordures ménagères, les cendres volantes de charbon, les REFOM etc., demeurent des matériaux de première importance pour l'évaluation environnementale, mais la liste sera très dépendante des usages faits dans chaque pays.

Il en est de même pour les scénarios. Par exemple pour les Pays Bas, les résidus minéraux secondaires sont souvent réutilisés, en raison notamment du contexte géologique et géographique du territoire qui se traduit par un faible nombre de possibilités de stockage et une lutte continue pour conserver les surfaces conquises sur la mer.

Plusieurs thèmes ont émergé des discussions de ce séminaire comme devant faire l'objet d'un effort de recherche tout particulier. On pourra citer :

- Prendre en compte l'importance de prendre en compte le rôle de la matière organique dans le comportement des polluants.
- Comprendre le développement de la micro-fissuration dans les déchets monolithiques et l'interaction entre phénomènes mécaniques et chimiques.
- Définir comment évaluer la durabilité et à partir de quels critères ?
- Comment aborder une approche plus globale, de type Analyse de Cycle de Vie, en tenant compte de phénomènes complexes de spéciation chimique ?

- Est-ce que l'étude d'analogues naturels peut aider à appréhender les impacts à long terme ?

- Physical and chemical evolution of parent materials.
- "Type curves" of leaching behaviour, characteristic of certain classes of materials.

4.4. ON WHICH ASPECTS SHOULD EFFORTS CONCENTRATE?

Regarding this issue, the discussion remains open. It is clear that cement materials, municipal solid waste incineration bottom ash, bottom ash and exhaust gas residues from household waste incineration, fly ash from combustion plants etc., remain materials of utmost importance for environmental assessments, but the list is extremely dependent on practices in each country.

The same applies to scenarios. In the Netherlands for example, secondary mineral residues are often reused due to the countries specific geological and geographical context which implies few opportunities for landfills and a continuous struggle to preserve land gained on the sea.

Several themes emerged from the discussions during this workshop as particularly worthy of research efforts:

- Taking into account the influence of organic matter on pollutant behaviour.
- Understanding the development of micro-fissures in monolithic waste and the interaction between mechanical and chemical mechanisms.
- Define how to assess durability, with which criteria.
- How to adopt a more global approach as in Life Cycle Analysis, taking into account complex chemical speciation phenomena?
- Can natural analogs help to predict long term impacts?

Annexe 1

Communications extended abstracts (Communications résumés étendus)

RECENT DEVELOPMENTS IN CHARACTERISATION LEACHING TESTS AND GEOCHEMICAL MODELING TO DEFINE A SOURCE TERM FOR ASSESSMENT OF ENVIRONMENTAL IMPACT

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Abstract

An integrated framework of environmental impact assessment of a wide range of constituents, in a wide range of materials and for a wide range of utilization and disposal scenarios is presented that allows a wide range of questions on release behavior of materials to be answered.

Introduction

In Europe, regulations are in development in several policy fields to specify requirements for the release of contaminants to soil and groundwater. Among these are construction products (Construction Products Directive, CPD), preserved wood (Biocide Directive), contaminated soil and sediments (e.g., in relation to the Water Framework Directive), landfilling of waste (Landfill Directive). In all of these fields, requirements for products must be coupled to testing methods with which the release of contaminants from products can be measured and modelled. As the aim in these fields is essentially similar, i.e., regulate release to soil and groundwater, it is essential that a unified approach is followed to avoid unnecessary duplicative testing and prevent potentially conflicting policies due to different requirements for the same material in different use scenarios.

During the past decades, many release test methods have been developed that attempt to simulate individual field conditions for a specific product. Most of these test methods are 'conditional' as their results only apply to a specified scenario (e.g. test simulating rainfall to quantify release of preserved wood). The consequence of such 'conditional' testing is that test results can neither be compared to results from other test methods, nor to results of different materials, and/or to conditions met in practice that are beyond the testing conditions. The absence of a common basis for judgement of a variety of products under a variety of conditions greatly complicates the development of common regulation criteria that any product has to fulfil. Therefore, the development of as many different test methods as there are materials and application scenarios, is an unnecessary costly and inefficient route.

Test methods alone are not sufficient as test results need to be linked to an assessment of impact, which implies that results obtained from leaching tests should provide the necessary information to describe a source term for impact modelling, as coupled chemical reaction-transport modelling is the only option available to provide insight in the long term behaviour of materials under changing exposure conditions in

the field. The use of more complex, detailed modelling can be balanced with the use of simplified, semi-empirical and semi-analytical models, which when knowingly over-predict release (i.e., are conservative), can be used for initial screening purposes. The results of such modelling can then be verified against field observations. In EN 12920 the sequence of steps from problem definition to verification between model prediction and field observation are indicated. A further worked out framework is given in Kosson et al (2002).

Here we want to focus on an approach that couples the wide variety of materials, the large number of potentially relevant constituents (inorganic-, organic parameters and radionuclides), the range of application conditions, the selection of testing methods, field observations, physical, chemical and biological factors in actual exposure conditions and regulatory criteria in an integrated framework of data storage, data comparison, modelling and interpretation.

Problems related to defining a source term

In many impact-modelling approaches a constant source term is applied, which in many cases is not a proper representation of the long term leaching behaviour. Often a limited set of constituents is taken along in the modelling. More complete and mechanistically-based modelling is often necessary to achieve improved understanding of controlling processes and make more realistic (less overly conservative) estimates of long-term release and performance. Based on the current full element modelling, it is clear that there are more inter-element interactions that can not be ignored. For instance, when Pb is modelled it can not be done without taking into account Fe-oxide sorption, interaction with DOC (dissolved organic carbon) and POM (particulate organic matter), as well as Mo and V, which form leadmolybdates and vanadates in many matrices. Several of the aspects such as organic matter interaction, redox changes, gas reactions (volatility, carbonation and oxidation), pH changes are not considered. Such simplifications are often applied to reduce the complexity of the required calculations. In many source term descriptions for impact modelling independent release functions are applied for individual constituents, thus negating the effect of interactions between elements and changes in mobility due to significant changes in solubility controlling factors. In virtually all soil and groundwater impact models a K_d type of interaction is applied to describe coupled reaction and transport, when for many cases several processes (including non-linear sorption, precipitation/dissolution, aqueous phase complexation/chelation, orthogonal diffusion) are responsible for actual behaviour and cannot be reasonable represented by linear equilibrium sorption.

A challenging new approach is to take along as much complexity as present models can handle, which presently implies taking into account mineral solubility, sorption to Fe and Al oxides, interaction with dissolved and organic matter, incorporation in solid solutions, changes in pH and redox as a result of atmospheric exposure, biological degradation or biologically mediated conversion, physical aspects such as particle size, permeability, preferential flow aspects, organic matter degradation, gas intrusion under varying degrees of saturation. Current computational advances, both in hardware and software, now make this approach practical for many applications.

Status of standard development as methods for source term characterisation

In CEN/TC 292 (Characterisation of waste) test methods have been and are still being developed for characterisation of the leaching behaviour of granular and monolithic materials. For granular materials the main characterisation methods have been finalised. For monolithic materials the standardisation process is still ongoing. In recent studies, the combination of a pH dependent leaching test and a percolation test (granular) and a dynamic monolith leach test (type of tank test for monolithic materials) has been identified as a suitable combination to derive the needed parameters for impact modelling. The pH dependent leaching test provides the necessary insight in the chemical speciation aspects, whereas the percolation test and the dynamic monolith leach test provide the time dependent release characteristics. The suitability of these tests for a much wider range of materials has been shown by the standardisation of very similar methods for leaching of soil and soil like materials in ISO/TC190 (Soil). More recently, the test methods have been proposed for the evaluation of construction products under the Construction Products Directive (CPD). This standardisation work falls under CEN TC 351 "Construction Products: Assessment of Release of Dangerous Substances". The advantage of a horizontal (defined as covering different fields which in CEN until now have seen independent development of tools) approach in testing to assess a time dependent source term is that no double testing is needed when a material switches categories (i.e. changes from a waste into a product and vice versa). Through geochemical modelling a description of the source material can be provided, which can be used as input in a chemical reaction transport model that allows prediction of release in a give utilisation or disposal scenario. While standardization to date has focused on test methods, standardization is also necessary for data management, presentation, modelling and interpretation. Decoupling of testing from use of the test results often results in misinterpretation and misrepresentation of the results. In the United States, USEPA is working towards adoption of the integrated leaching assessment framework, including test methods, data management, scenario modelling and interpretation as part of official guidance and standard methods.

Based on the modelling experiences recommendations for test modification (pH range in the pH dependence leaching test) as well as suggestions for additional standardised test methods can be made (Fe and Al oxide surface quantification, DOC and TOC fractionation for reactive fraction for metal sorption, redox capacity test, compacted granular leach test for non-permeable granular materials)

Developments and approach in source term modelling

For geochemical speciation/ transport the modelling framework ORCHESTRA (Objects Representing CHEmical Speciation and TRANsport models) is used (Meeussen, 2003), which is embedded in the database/expert system LeachXS. The latter forms the integrated approach that allows linking various aspects of materials together. Proper thermodynamic stability data and other solubility controlling parameters (Fe-oxide, Al-oxide, dissolved organic carbon and particulate organic matter) are crucial for the above indicated complexity in modelling to be successful.

Within this system the following subsequent steps have been developed:

- Measurement of constituents with pH dependent leaching test on granular material or size reduced monolithic specimen (chemical speciation aspect).
- Measurement of release of constituents by percolation as a function of L/S (liquid/solid ratio) or as a function of time from monolithic materials (dynamic release)
- Prediction of the pH dependent release based on a set of selected minerals, sorption on Fe and Al - oxides, interaction with dissolved and particulate organic matter and incorporation in solid solutions (chemical speciation fingerprint).
- This chemical speciation fingerprint is used in combination with transport in a percolation scenario with dual porosity to describe the outcome of the laboratory test.
- This chemical speciation fingerprint is also used in combination with transport from a monolithic material by taking into account leachant renewal cycles, continuous renewal, product tortuosity (measure for porosity and pore structure)
- When a satisfactory prediction is obtained for the chemical speciation fingerprint and for the time (or L/S) dependent release, the material can be assumed to be well characterised over a wide range of pH and time or L/S conditions relevant for long term behaviour. The chemical speciation fingerprint of the material can then be used as the basis for reactive transport modelling to predict release under well-defined field scenarios with external influencing factors, such as carbonation (CO₂ uptake), redox change, degree and variation in water contact.

An integrated system for leaching testing and evaluation is under development as LeachXS. The integration of data storage in a unified data format to facilitate easy comparison of the wide range of laboratory data, lysimeter data and field data, a scenario database to facilitate environmental impact evaluation under different exposure conditions for different materials, a regulatory database with judgement criteria for different utilisation and disposal options, a thermodynamic database for speciation modelling and a chemical reaction transport code (Orchestra) in a model that facilitates data retrieval, model input and post modelling data processing creates new possibilities for the use of speciation information in the decision making process.

Although this paper focuses on inorganic constituents (metals and oxyanions), the principles largely apply to organic substances and radionuclides as well, as far as their release to the water phase is concerned.

Modelling examples

Some examples of modelling possibilities are highlighted below to give an impression of the capabilities of this robust approach and the LeachXS system.

Judgment of granular materials

The judgment of leaching behaviour on any material based on a single extraction is impossible without understanding the relationship of that test result with the practical situation to be judged. Arbitrary choices of a test condition can be overprotective for some constituents, but at the same underpredicting effects for others. In figure 1, the relationship between the proposed characterisation test for granular materials (pH dependence and percolation) with compliance test data, other tests and regulatory

criteria is given. Because the information contained in these four graphs covers many possible exposure conditions, it covers probably more than 80 % of the applications of the material considered. The presentation of results in mg/kg allows a conclusion on the consistency of the end point of the percolation test and the pH dependence test at the corresponding pH. It can be seen that tests with a different L/S relate to different aspects when presented in either mg/kg or in mg/l, making data presentation using both bases (mass and concentration) useful. As can be seen here for Cu leaching from MSWI bottom ash, the maximum leached amount is approached within L/S =1, similar as for salts. From other work it is known that that is related to the association of Cu with DOC, which in complexed form is readily washout. The BSE (Soil saturation test; Germany) is carried out at low L/S. Obviously, it can not be related to an L/S =10 method as it focuses on the low L/S range. After carbonation the Cu leaching is not significantly changed. Comparison with regulation can be made by taking the relevant pH domain into account. The upper pH is the own pH of the material and the lower range is the pH that results after carbonation (here 7.8). The upper limit of the judgement box in the pH dependence test graph is the regulatory limit. The lower limit is the detection of determination limit of the parameter considered. In the graph on Cu leaching from MSWI bottom ash it is also clear that bottom ashes produced in Germany, France, Austria, Taiwan and the Netherlands are showing the same leaching character (in pH dependence as well as in percolation test). This shows that MSWI bottom ashes generated in different installations worldwide have the same basic leaching behaviour, which opens the possibility to define the reference behaviours of incinerator bottom ash against, which less elaborate data can be judged.

Below a few examples of leaching behaviour of granular materials is given following the same basic approach.

Municipal solid waste incinerator bottom ash

As indicated before MSWI bottom ash leaching behaviour is very consistent worldwide. By using chemical speciation modelling the mineral phases and sorptive phases controlling leachability can be identified and quantified. In table 1 the input parameters for the model are indicated.

Soil

In figure 3 the partitioning of zinc and copper between dissolved and particulate phase is given. The role of dissolved and particulate organic matter to describe Zn and Cu leaching behaviour properly is obvious. The very sharp gradient between pH 5 and 7 in the distribution of Zn and Cu in DOC bound and free Zn and Cu is of importance for plant uptake, uptake by biota and of relevance for transport to subsoil and groundwater.

Compost

In figure 4 a model prediction for green compost CW5 (source separated household waste) is given with the partitioning between dissolved and particulate phases. The relevance of dissolved and particulate organic matter is quite obvious for this matrix. The partitioning as observed is driven mainly by the dissolved organic matter concentration.

Coal fly ash

In figure 5 the simultaneous prediction of more that 25 elements in a percolation test are shown. This modelling option has been recently developed and still needs further improvement. The model includes dual porosity and takes into account minerals and Fe oxide sorption.

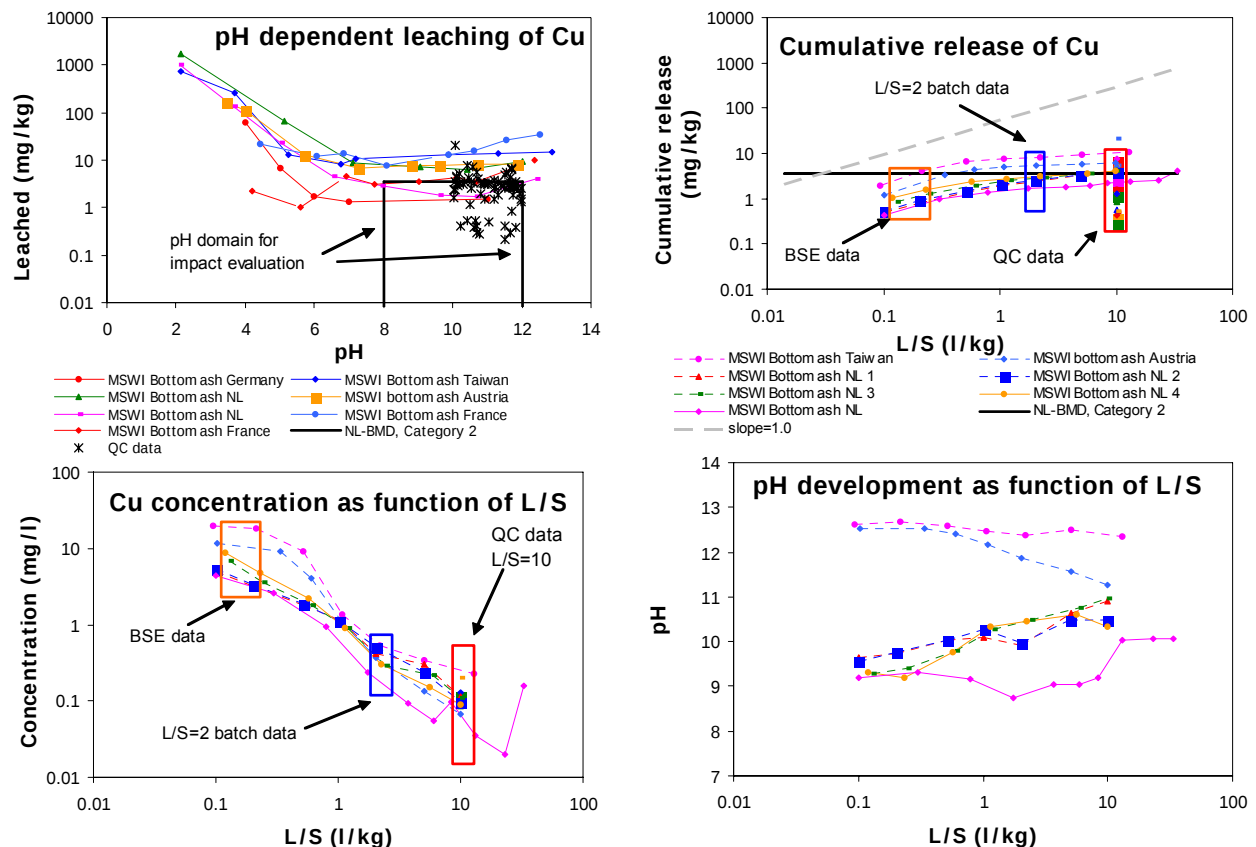


Figure 1. Integrated evaluation of characterisation leaching test data for granular materials consisting of pH dependence test (CEN/TS 14429) and percolation test CEN/TS 14405).

Table 1 Input parameters for speciation modelling.

[illegible]

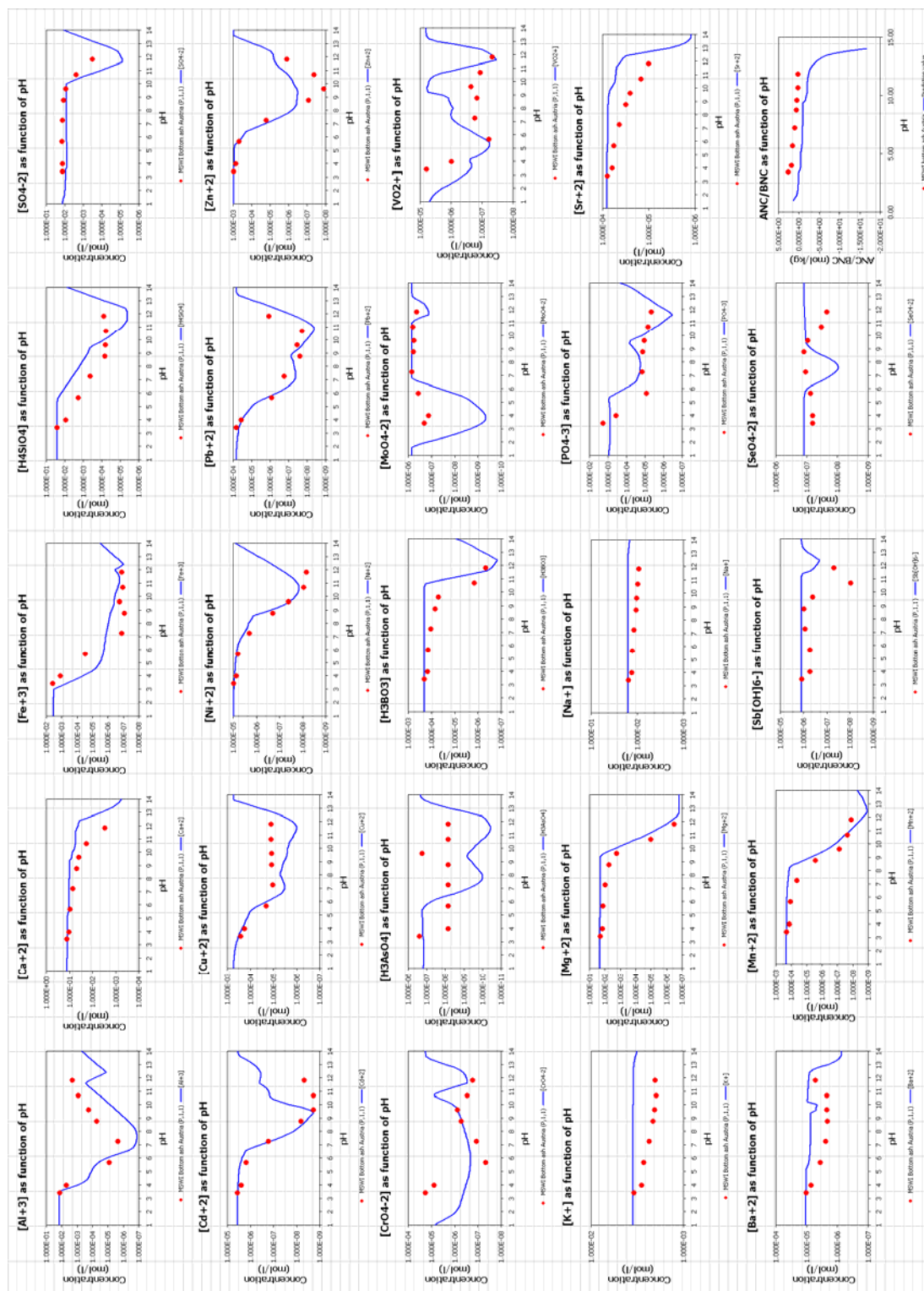


Figure 2. Prediction of major, minor and trace elements from MSWI bottom ash leaching based on input data from table 1 in comparison with pH dependence test data (TS14429).

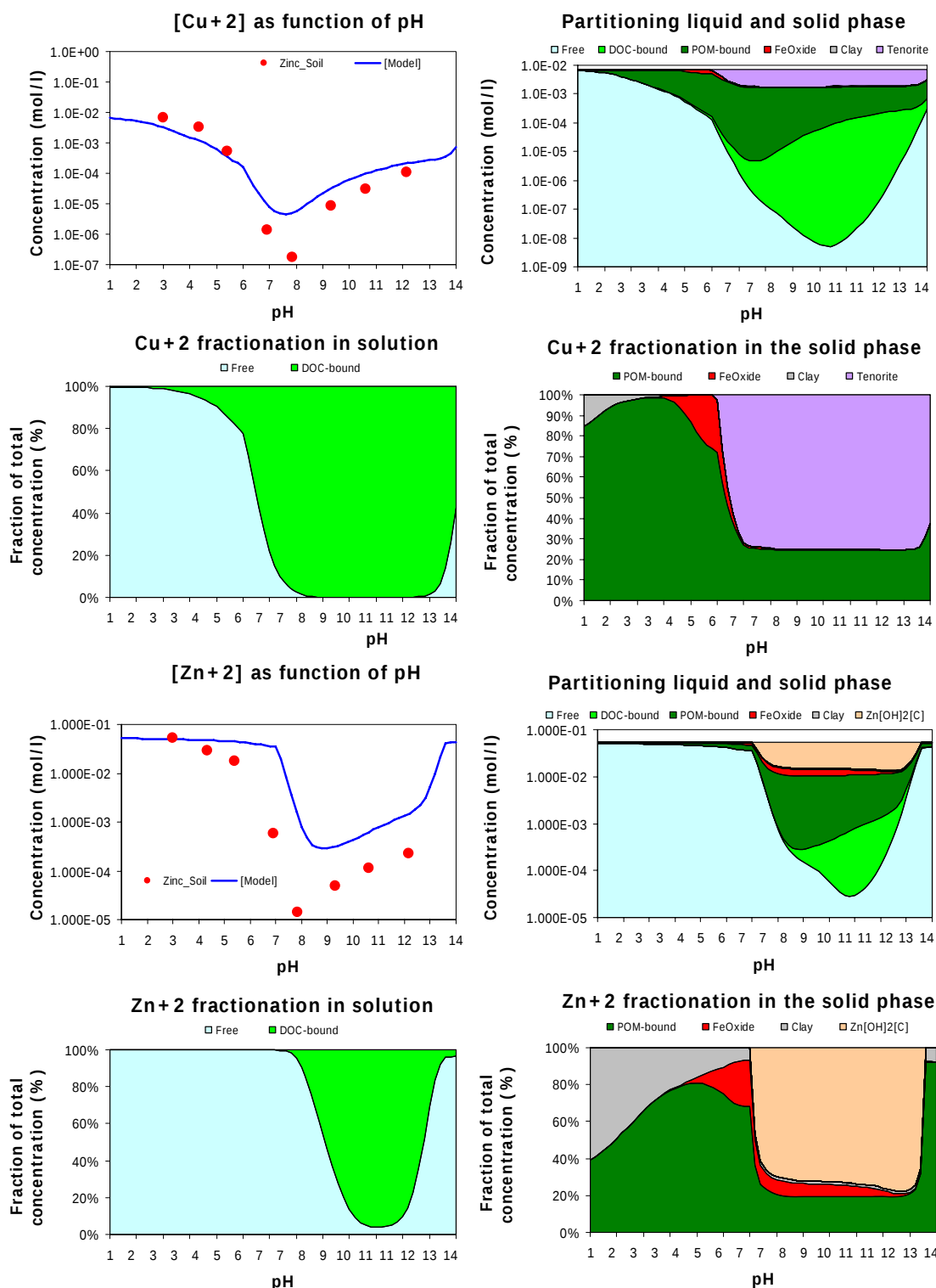


Figure 3. Model prediction of pH dependence test data and partitioning of Cu in dissolved and particulate phases for a zinc contaminated soil.

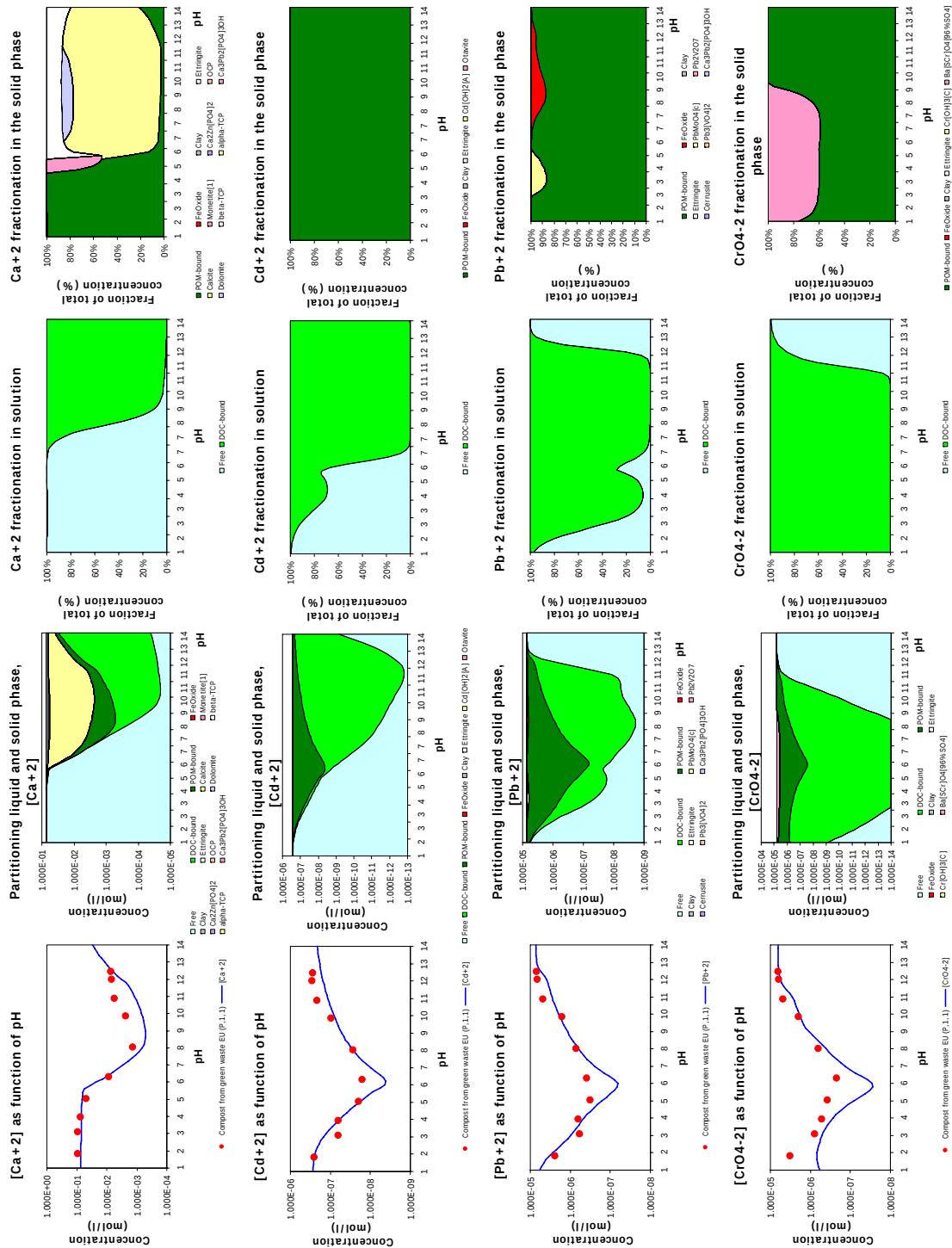


Figure 4. Prediction of pH dependence test data for Ca, Cd, Pb and Cr for green compost (CW5) with partitioning between dissolved and particulate phases.

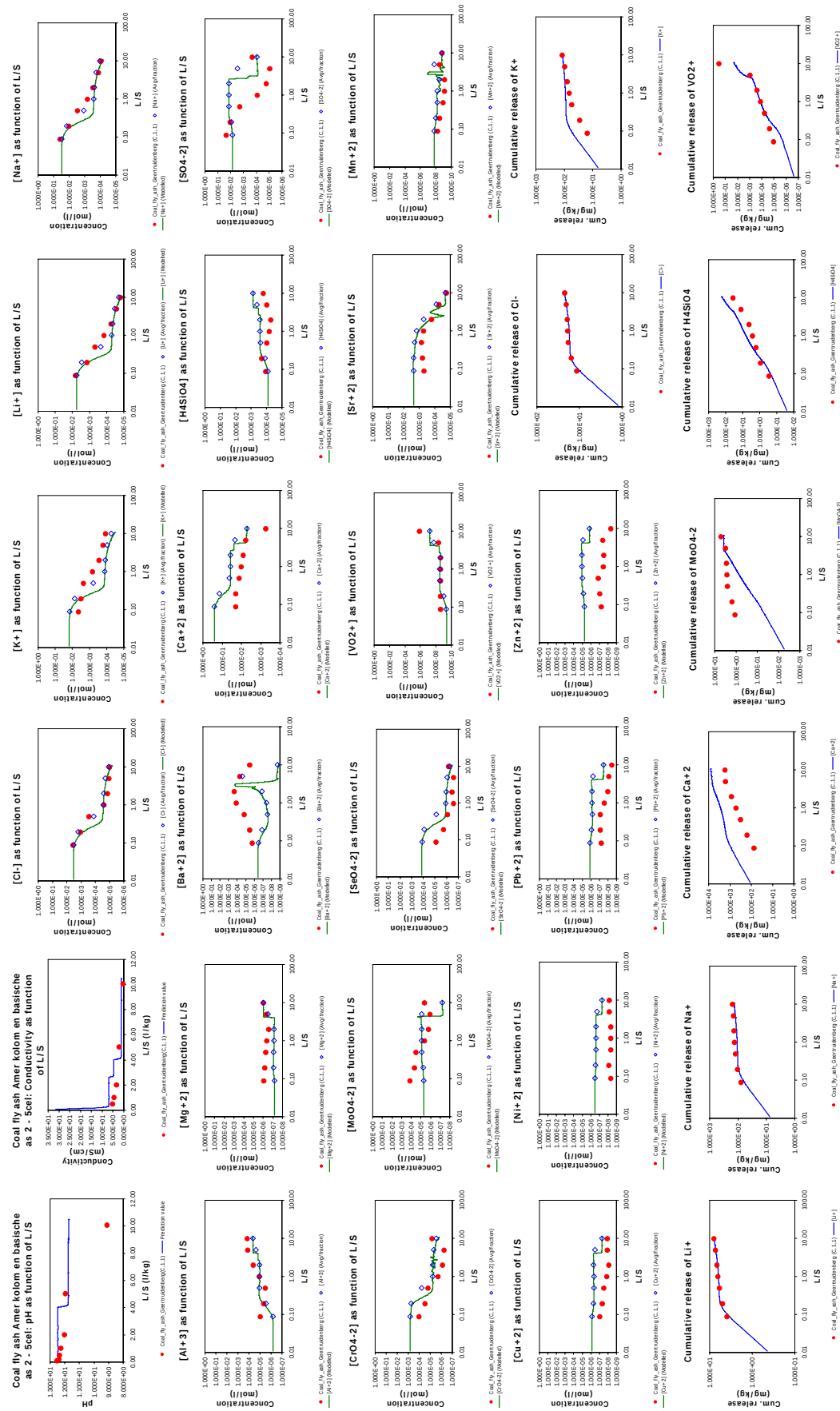


Figure 5. Prediction of percolation test data for coal fly ash in comparison with the test results obtained by TS 14405.

Judgment of monolith leaching

The basic concept for the prediction of tank leaching test results is similar to the approach followed for granular materials. In this case the pH dependence test provides the chemical speciation fingerprint (figure 6). Here a Portland cement mortar NOR2 has been tested using TS 14429 on crushed material and a dynamic monolith leach test with leachant renewal (ECRICEM II project). The results of the prediction of the monolith test are given in figure 7 in comparison with the actual measurements. The model required very thin cells at the interface to account for the very large concentration gradient at the interface, which creates too large mass transfer between cells leading to stability problems. Once the leaching has progressed the interface concentrations change and the calculations become more stable. In figure 8 the porewater concentration profiles are given as a function of time at a specified depth into the product and as a function of depth at a specified time for NOR 2 at own pH. This provides insight in the complexity of the mineralogy at the interface. The pH prediction is crucial, which implies that the set of selected minerals must be right. The salt release is controlled by tortuosity, this factor is product specific and is obtained from the tank test. The next step is to get the major elements right. This generally requires a good balance between Al, Si and Ca. In figure 9 the porewater concentration profiles are given as a function of time at a specified depth into the product and as a function of depth at a specified time for NOR 2 after carbonation.

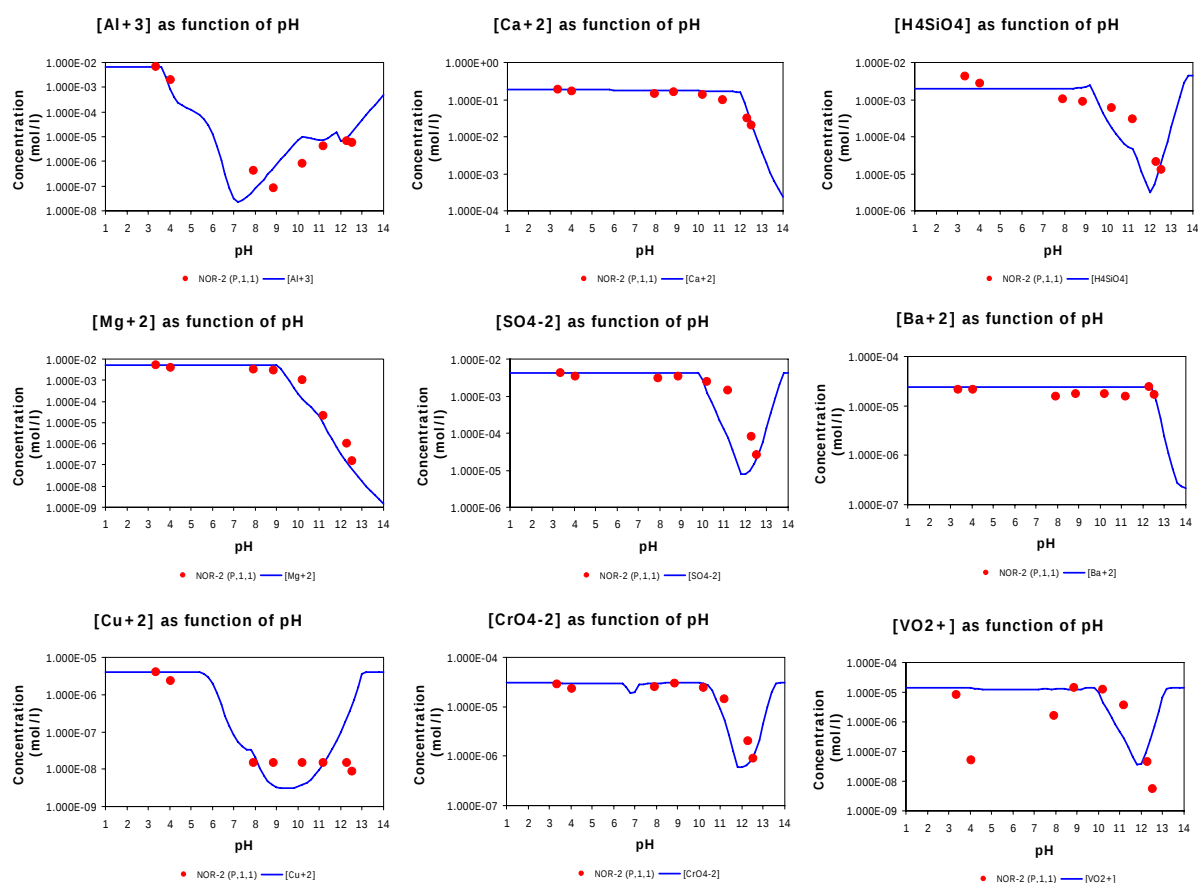


Figure 6. Prediction of a selection of major, minor and trace element leachability in pH dependence leaching test for cement mortar NOR2.

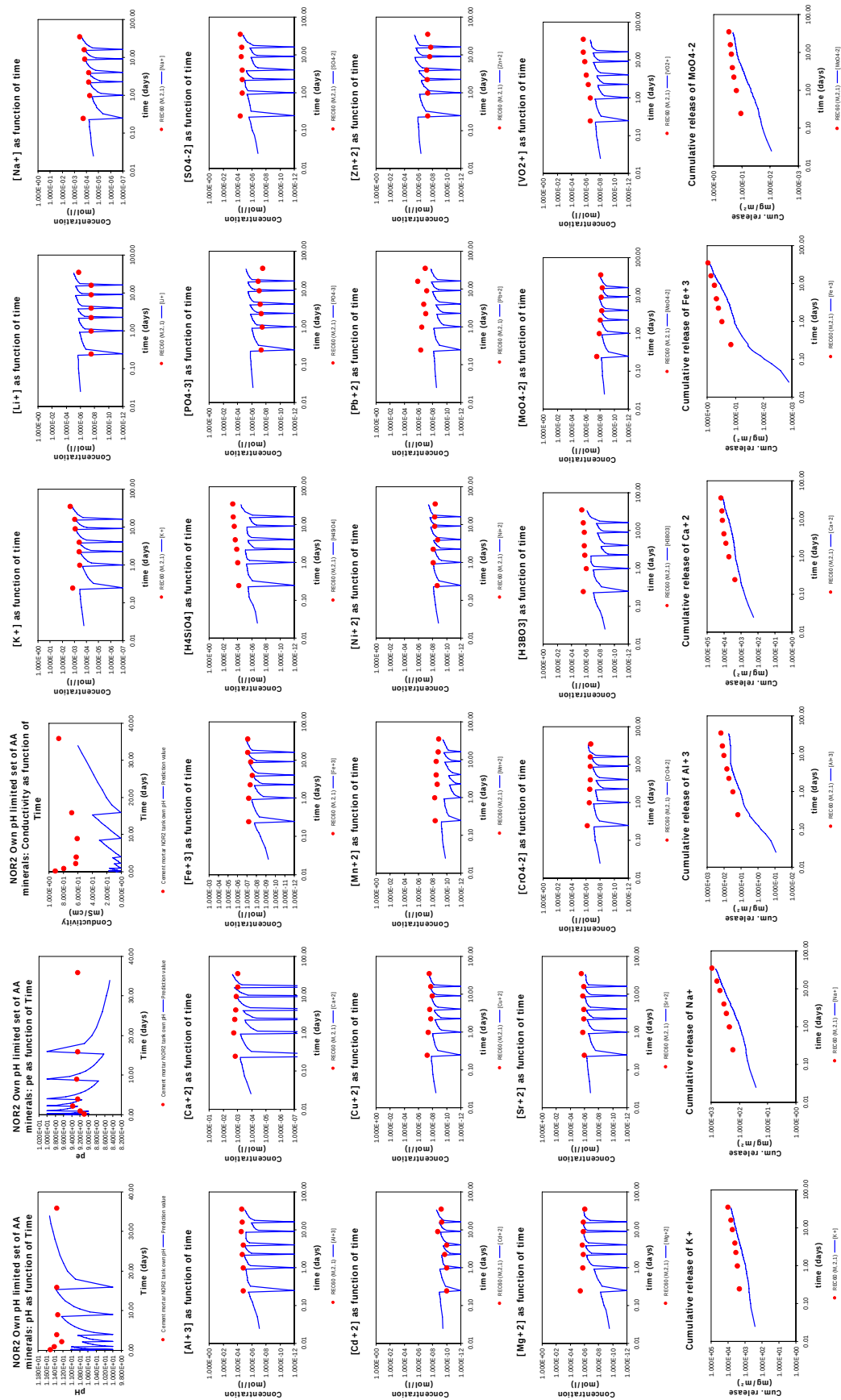


Figure 7. Prediction of release of major, minor and trace elements from a Portland cement mortar in comparison with the actual test data.

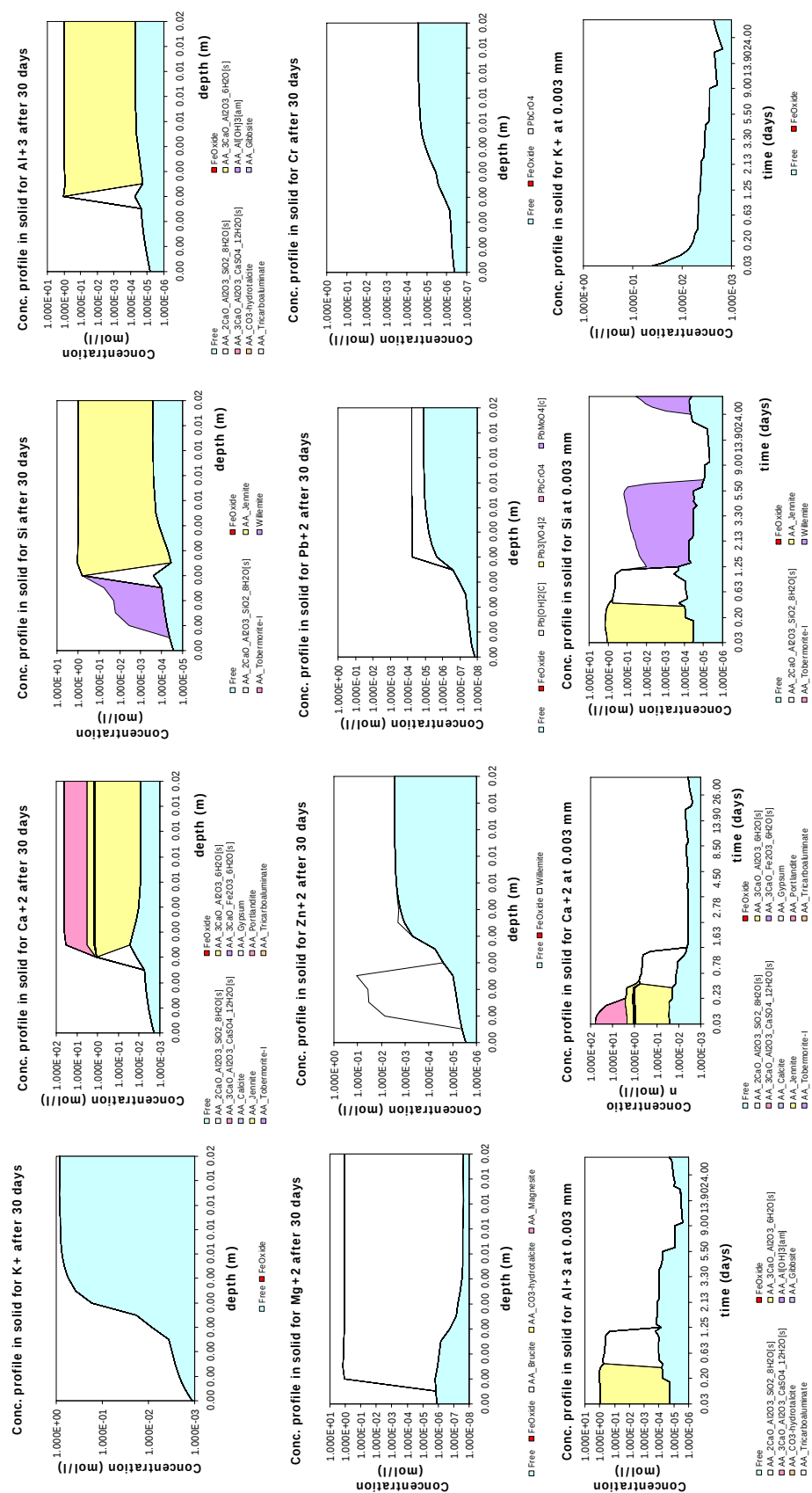


Figure 8. Concentration profiles as a function of depth and as a function of time for cement mortar NOR2 at own pH

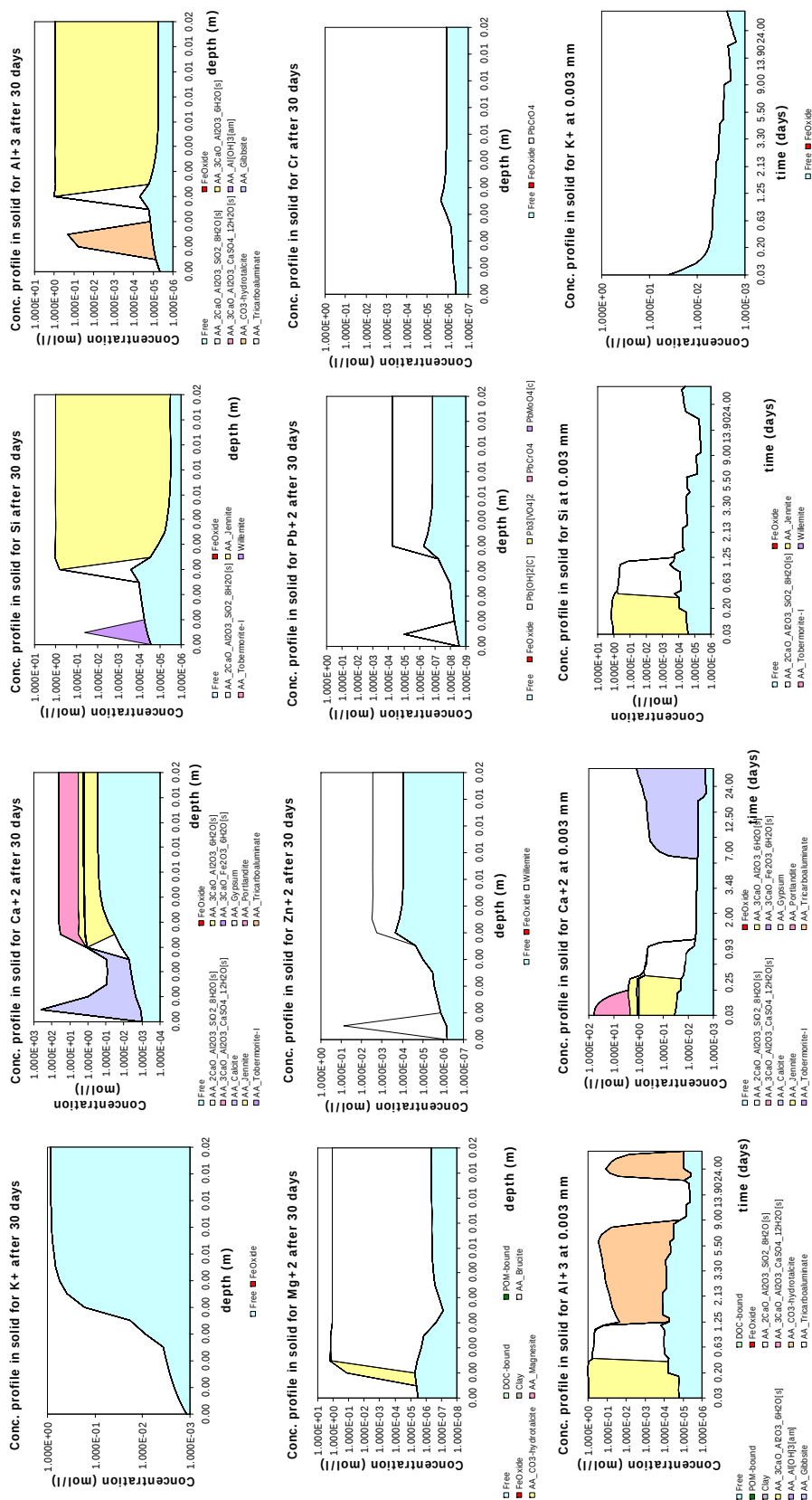


Figure 9. Concentration profiles as a function of depth and as a function of time for cement mortar NOR2 after CO₂ exposure.

Conclusions

The characterisation leaching test methods developed in TC 292 for waste are equally applicable to a wide range of other materials, which implies that horizontal standardisation of characterisation leaching tests is feasible. A recommendation for validation of these methods covering a wider range of materials than just waste was forwarded as a recommendation from SABE (Strategic Advisory Body on Environment) under CEN STAR to DG Research for support.

An integrated approach of assessing environmental impact for broad range of materials and products is the way forward, as developing tools for individual fields is leading to unnecessary duplication of work. The better understanding of material behaviour as derived from more elaborated characterisation will provide better means to find solutions to material improvement, proper information on a source term that can be used for impact evaluation in a variety of exposure scenarios, a bench mark for typical materials, as materials produced in a specific type of facility is likely to show a common leaching behaviour, and allow placement of other (more limited) test data in perspective.

The developments in modelling provide insight in the capabilities and limitations of standard test methods. In fact optimisation of present methods can be suggested to even better match them with the test objective (pH 2 step in pH dependence test for better availability estimate, wrap column in Al foil to reduce bioactivity, use N₂ flush to prevent neutralisation of high pH leachates). From the modelling work it is also clear that additional methods or protocol are needed for specific material properties, that are crucial in understanding leaching behaviour (e.g. DOC fractionation, quantification of Fe and Al sorptive surfaces)

The insight in release controlling processes also provides better means to derive compliance procedures by finding the more sensitive condition of testing. By placing compliance test data in conjunction with characterisation test data further reaching conclusions can be drawn on limited testing. This calls for availability of characterisation data in a widely assessable database. Worldwide large amounts of leaching data are available, as illustrated here MSWI bottom ashes from around the world exhibit the same basic character. This should be exploited further as it will help to avoid unnecessary duplication of work. The source term as derived from the chemical speciation fingerprint, that can be derived from the pH dependence test has been shown to be very suitable for prediction of different laboratory test results, as starting point for impact modelling, for evaluation of material mixes and as basis for assessing multilayer scenarios. The full mechanistic modelling approach presented here is an ambitious approach, but given the current capabilities it definitely seems the best way forward to environmental impact modelling. Further development will be focussed on building new scenarios and the verification of field observations against model predictions.

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LeachXS - Database/expert system www.leachxs.com

Validation of leaching tests - a key issue towards reliable use of results

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Abstract

Interlaboratory comparisons have been carried out to evaluate the reproducibility of different laboratory procedures for the determination of source term strength of pollutants in soil and waste materials.

Partly modified existing standards and guidelines for elution, extraction and column percolation tests were used. The leaching behaviour of PAHs, copper, chromium, sulphate and chloride was evaluated based on three reference materials. Parameters such as DOC content, pH value, conductivity and turbidity were included in the evaluation.

While reproducible results were obtained for the elution and extraction tests for inorganic parameters, the situation was different for PAHs. The interlaboratory comparisons using column tests provided reproducible results both for inorganic parameters and for PAHs despite different column dimensions in the participants' experiments. Special emphasis was placed on a uniform contact time between soil and leachant during the column experiments as well as stipulations for filling the columns with the materials. Thus column tests can be regarded as a suitable instrument for the source term determination for leachate prognosis with appropriate stipulations.

Introduction

The leaching behaviour with respect to groundwater compatibility has to be tested, especially when waste materials are tipped on the ground and detrimental changes to the soil might occur. The Federal Ordinance on Soil Protection and Contaminated Sites (BBodSchV) [1] requires a risk assessment based on a "leachate prognosis" procedure for the soil-groundwater pathway in Germany. Laboratory leaching tests may be used for source term determination in combination with model calculations.

Since 1999, an integrated R&D programme "Leachate prognosis" funded by the German Federal Ministry for Research and Education (BMBF), has promoted research projects in this field [2]. One of the aims of the joint project is the development of suitable methods for the determination of the pollutant source strength in order to acquire the necessary forecast data. Within the framework of a central project BAM carried out the processing of three materials with a defined source strength for certain pollutants (reference materials) in order to ensure comparability of the results of the participants of the integrated programme. Bottom ash from MSWI, contaminated soil and contaminated demolition waste were selected as waste materials. 6 tons of each material was processed and delivered to the partners in aliquots from 15 to 1200 kg for

laboratory tests up to large lysimeter tests [3]. Additionally interlaboratory comparisons on the evaluation of the reproducibility of different existing laboratory leaching tests at different liquid to solid (L/S) ratios were conducted using the three waste reference materials [4].

There are a number of methods available for laboratory tests (column experiments, batch tests, tank tests, extractions), however, depending on the equilibrium condition attained, the results of the experiments are difficult to compare. Currently there is a lack of reliable and comparable leaching methods especially for source term determination of organic contaminants.

The most commonly applied leaching tests in Germany are batch tests with different L/S ratios, the so called soil saturation extract test for inorganic contaminants and column tests preferable for organic contaminants. In general, lysimeters are used for large scale investigations and are appropriate to gain data under field conditions; however, they are not applicable as a routine procedure.

Interlaboratory comparisons

Procedures

Some laboratories and institutions of the integrated project participated voluntary in the interlaboratory comparisons.

First special procedure guidelines based on existing standards had to be developed. Leaching/extraction and percolation tests were carried out at following basic conditions:

- Batch tests in accordance to DIN EN 12457-1:2003-01, DIN EN 12457-2:2003-01, ISO DIS 21268-1: 2004-06, ISO DIS 21268-2: 2004-06 and DIN 38414-4:1984-10

L/S ratio	2 or 10 l/kg dry matter
Sample net weight	0.25 kg or 0.125 kg
Leachant	demineralized water
Agitation step	overhead tumbler 3 rpm, 24 h, 30 min sedimentation
Filtration step	decantation, pressure membrane filtration 0.45 µm

- Modified soil saturation extraction tests following BBodSchV [1]

L/S ratio	0.25 l/kg dry matter
Sample net weight	0.25 kg
Leachant	demineralized water
Contact time	Stirring until complete wetting, equilibrium adaptation of 24 h at 5°C
Filtration step	Cooled centrifugation 3000 rpm, pressure membrane filtration 0.45 µm

- Column tests using an experimental set-up in accordance with DIN CEN/TS 14405:2004-09 or ISO DIS 21268-3:2004-09 with a pre-defined contact time and filling method

L/S ratio	increasing up to approx. L/S = 6 l/kg
Leachant	demineralized and degased water, 5 mg/l Na ₃ N added
Contact time leachant/sample	approx. 14 -18 h
Ambient conditions	20°C ± 5°C, dark room
Leachate preparation	no filtration or centrifugation

During the column experiments special emphasis was laid made on a uniform contact time between soil and leachant as well as instructions for filling the columns with the materials since participants were allowed to use columns of different dimensions. Columns with internal diameters of 40 to 90 mm with fill heights between 12 and 30 cm were in use. These dimensions suggested sample masses of between 0.5 to 3 kg and flow rates of between 0.11 to 0.5 ml/min when the necessary contact time was adhered to. The participants were able to achieve the specified dry densities using the placement method as suggested with tolerable deviations. Glass columns were used, except in one case where high-grade steel columns were used. The materials had to be placed in “dry” condition into the columns. Before starting the tests the columns filled with the sample material had to be saturated rapidly. Immediately after saturation the column percolation tests had to be continued with the flow rate determined for the respective test. The flow rates to be applied had to be calculated based on the column dimensions and bulk densities of the samples achieved during placement in the columns. The test duration needed by the participants was within 8 to 25 days. With increasing experimental time the time intervals of the sampling should be increased. For the unification, L/S ranges were specified within which samples had to be taken.

Separate tests (double tests each) had to be performed for the investigation of inorganic and organic constituents for all leaching procedures. Since the modified soil saturation extraction tests provide only a small volume of leachate this test was only applied to investigate inorganic constituents.

The measuring program to be performed on the percolates included pH value, conductivity, turbidity, DOC content. Chloride, sulphate, copper and chromium were analysed for RM demolition waste and RM MSWI bottom ash. PAHs were measured in the eluates of RM soil and RM demolition waste.

Results and discussion

A statistic evaluation for the interlaboratory comparisons based on the column percolation tests was differing to conventional round-robin test evaluation since there were no uniform points of reference to certain L/S ratios due to individual laboratory's differences in sampling times. Therefore the column percolation tests were evaluated based on a graphical illustration of the test results. The evaluation of the batch and extraction tests were performed in accordance to DIN 38402-45:2003-09 and ISO 5725-2:2002-12.

Whereas column tests provide good reproducibility for inorganic and organic substances, in batch tests the reproducibility was generally satisfactory except for the PAHs.

During batch tests the filtration step, i.e. the separation of the leachate from the solid sample, generally seems to be the critical step in the sample preparation procedure for the subsequent analytical measurement and was responsible for the reduction of the measured PAH concentrations. The filtration step was less critical for the analysis of inorganic constituents.

Compared to the results of batch tests, the interlaboratory comparison on column tests mainly showed good reproducibility of the participating laboratories both for the investigated substances and the accompanying parameters. Even for PAHs there was a good agreement for the column test releases within the participating laboratories as well as between the labs. The consistent contact time between eluent and sample material as well as stipulated sample placement procedure applied by all participants is above all assumed to contribute to this good agreement. Furthermore no additional liquid/solid separation step was performed.

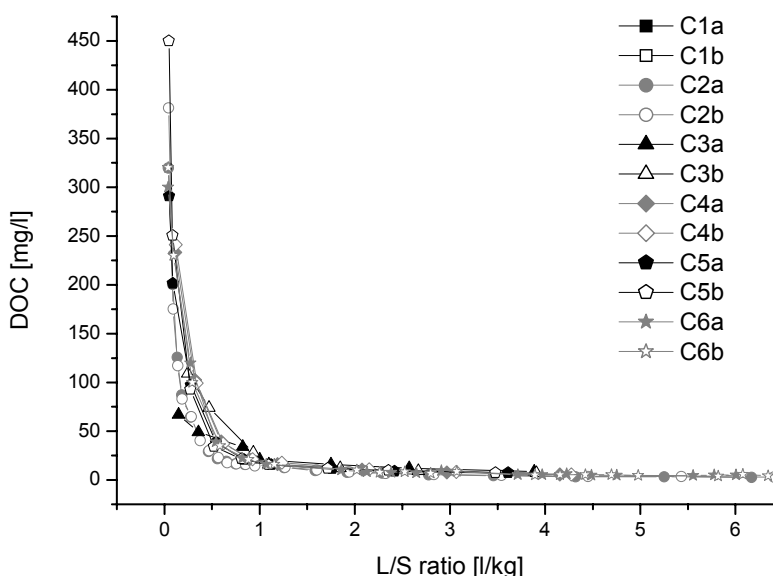


Figure 1: DOC contents of the inter-laboratory comparison of column percolation tests on demolition waste RM of participants C1 to C6 (two simultaneous tests a and b)

Figure 1 shows an example of good agreement of the curves measured by the individual participants (Laboratories C1 to C6) for the accompanying parameter DOC content in the column percolates of demolition waste RM. Figure 2 shows the good reproducibility of the determination of inorganic parameters using the example of concentration and cumulative chromium release for MSWI bottom ash RM. The release of the PAH sum is shown in Figure 3 by the example of soil RM. The figures indicate very good agreement of the two simultaneous tests a and b at the same time.

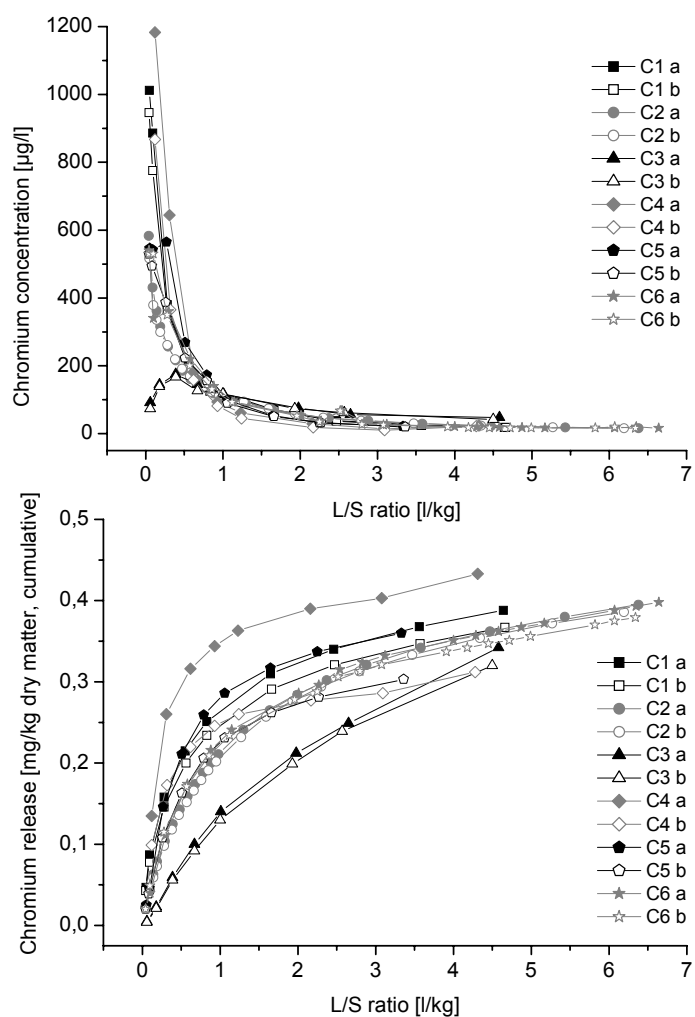


Figure 2: Chromium concentration and chromium release of the interlaboratory comparison of column percolation tests on MSWI bottom ash RM of participants C1 to C6 (two simultaneous tests a and b)

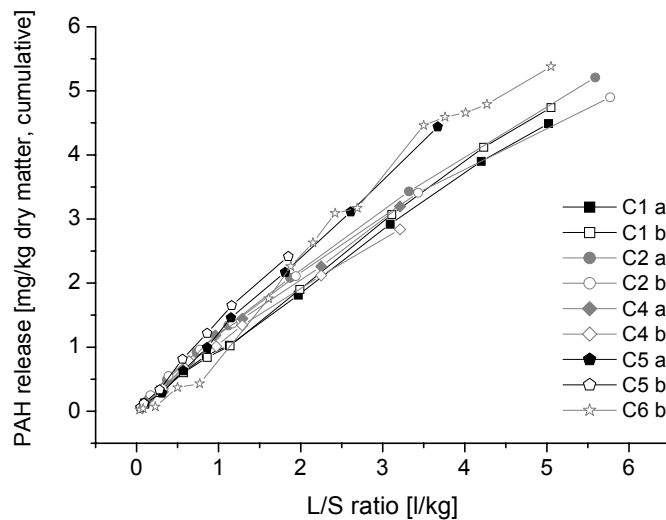


Figure 3: PAH release in the interlaboratory comparison of column percolation tests on soil RM of participants C1 to C6 (two simultaneous tests a and b)

Conclusions

Within the framework of this study guidelines were established for applied leaching procedures. Batch and extraction tests are generally appropriate for the investigation of leaching behaviour of inorganic compounds. However stringent stipulations must be provided, especially with regard to the eluate pretreatment before subsequent analysis. The column test guideline developed for the interlaboratory comparisons is proved to be fit for this purpose. Minor improvements might be necessary taking into account long-term experience (e.g. measures for prevention of biodegradation).

The investigations carried out will help to establish standardized and feasible laboratory procedures for source term determination and contribute to the harmonization of leaching procedures within the framework of a leachate prognosis for risk assessment of contaminated land.

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Re-use of waste and behaviour of heavy metals: a molecular approach of the transfer mechanisms

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Waste management: a crucial issue to preserve natural resources (soil and water) and to prevent atmospheric pollution.

The societal debate concerning wastes and waste management is periodically present in the media following the discovery of uncontrolled dump sites, installation of new incinerators or exportation of waste from rich countries to any developing country.

Waste management is a central issue of the sustainable development and in particular the global warming and the preservation of natural resources (air quality, soil and water). Indeed a correlation exists between waste management and greenhouse gas emission; For instance new incinerators adapted for heat recovery can help saving fossil fuels. Waste methanization is an other example for saving fossil fuels and fossil energy.

The stakes of the various waste treatment processes can be declined as follow: reduction of waste quantity, waste treatment, re-use and landfill. Such issues are strongly related with the French law from the 13-07-1992.

The CEREGE develops since more than 10 years a fundamental approach concerning the environmental impact of waste reuse mainly in civil engineering. The methodology is based on a molecular approach to characterize the mechanisms of toxicant release and transfer. Our approach is applied in many field of environmental sciences like water treatment, reuse of waste by the cement industry (co-firing), or the use of by-products from steel plants in road making. We will develop tree examples to highlight the force of the 'molecular environmental science'.

Methodological approach: molecular physical-chemistry at the solid-liquid interfaces.

The methodology consists in determining the atomic arrangement in highly divided solids and heterogeneous structures in order to predict the consequences in term of reactivity and pollutant fixation as well as the semi-local scale structure. We combine structural and chemical analysis at various scales using spectroscopies and microscopies. Indeed the study of reaction at a molecular scale is a really challenging and requires the combination of techniques analysing systems from the global, centimetric, micrometric down to the atomic scale. Various parameters can be determined:

- 1) Interatomic or inter-domain distances of meso-scale organised systems using **XRD** (X-ray diffraction) for the intra-crystalline order and SAXS (Small Angle X-ray Scattering) for the inter-particulate organisation, form, size, fractal dimension of objects. (**semi local-scale**).
- 2) Interatomic distances ($< 10\text{\AA}$) and speciation (including redox states) by combining XAS (X-ray Absorption Spectroscopy : XANES (X-ray Absorption Near Edge Structure), **EXAFS** (Extended X-ray Absorption Fine Structures)), X-ray **spectro-microscopies** (micro-XANES, micro-EXAFS), **FTIR** (Fourier transform Infra-red), **NMR** (Nuclear Magnetic resonance). (**local scale**)
- 3) Micro-chemical analysis using various microscopes **SEM-EDS** (Micro-analyse : Scanning electron microscope couple to EDS), **TEM-EELS-EDS** (transmission electron microscope coupled to Electron Energy Loss Spectroscopy et/ou l'EDS), **micro-XRF** (X-ray Fluorescence Spectroscopy).
- 4) Molecular modelling to infer the structural hypothesis obtained from experiments.

Of course our methodology is applied on altered matrix to determine the leaching behaviour of solid systems.

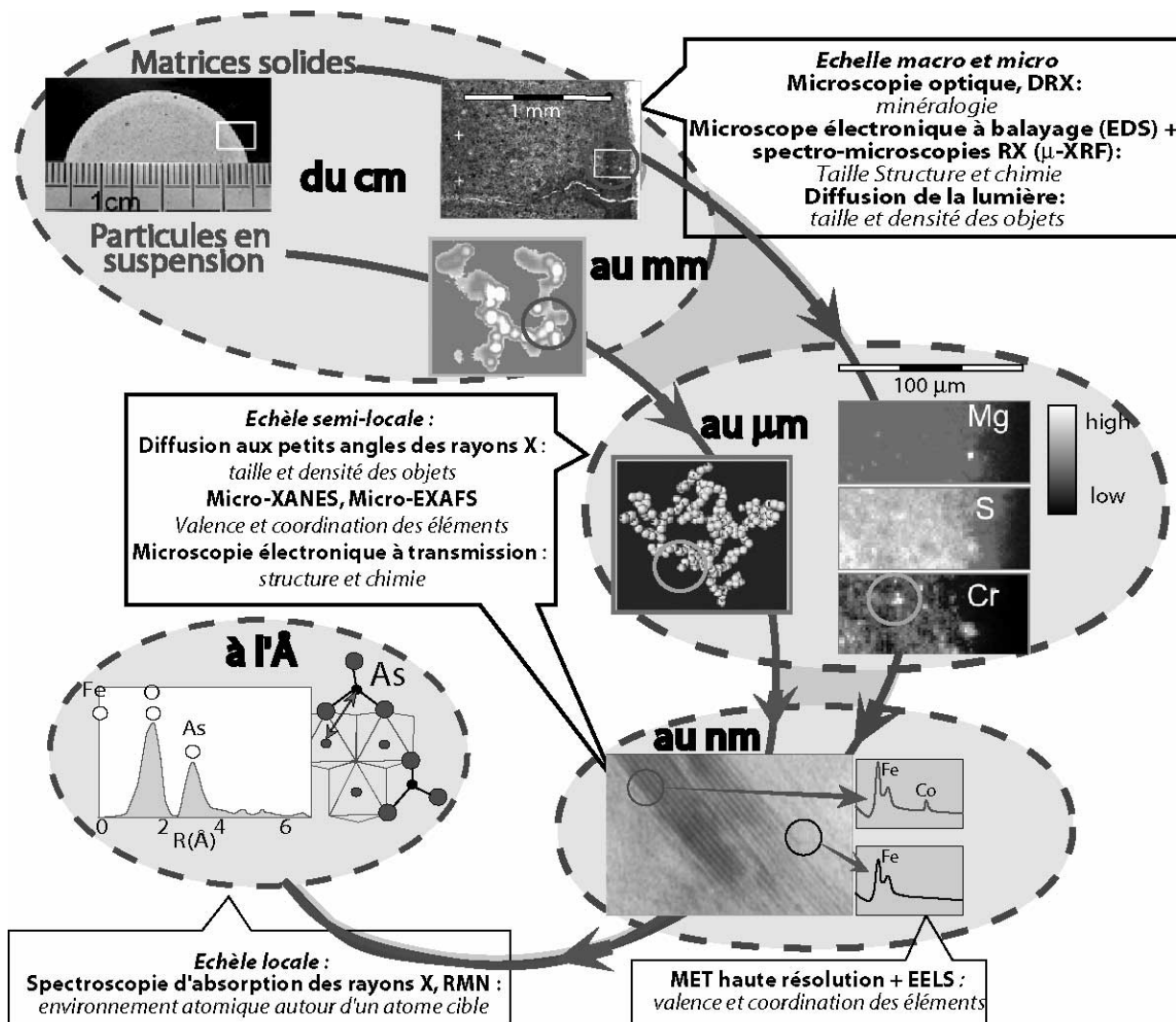


Figure 1 : Multi-scale structural analyse

Reactive transport models– long-term release mechanisms

Beyond the quantification of release rates, modelling is of primary importance for the understanding of long-term release mechanisms, and also for the extrapolation of laboratory results to site conditions characterised by lower solution/solid ratios, site specific geometry, cyclic infiltration, etc. Such models are based on a mechanistic description of the bio-geochemical reactions affecting the solid matrix during leaching experiment and determined by the molecular approach. This approach is developed in collaboration with Laurent DeWindt from 'L'école des Mines-Paris/Fontainebleau'.

Exemples

Fixation of heavy metals by hydraulic binder phases: impact of co-firing.

Cement industry has developed or adapted cement synthesis processes to re—use waste; First waste can be mixed with the raw material in order to be fired during the high temperature step. The second solution is to substitute fossil fuels by calorific wastes (paint, used lubricant...). The aim is to oxidize the organic matter which is more efficient than in conventional incinerator and to block inorganic toxicant in cement phases. The use of waste lead to a slight increase of the total amount of metal even if for each metal they can be considered as trace elements (Cr~ 65 mg/kg, Pb ~ 20 mg/kg (from ATHILH 2002)). In order to evaluate the safety of co-firing it is crucial determine the mechanisms of heavy metal fixation and release within the cement matrix.

Determination of heavy metal fixation sites during cement setting

Cement setting is due to the dissolution of initial anhydrous phases and the precipitation new hydrated phases. The evolution of the different initial anhydrous phases is summarized in the figure 2:

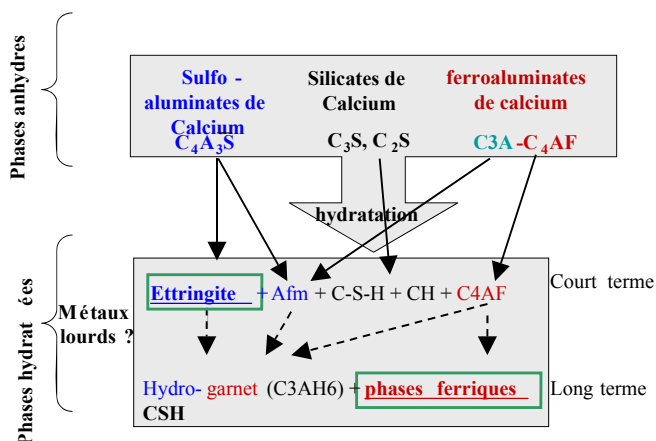


Figure 2: Hydration of cement anhydrous phases

$C_3S = (CaO)_3SiO_2$;
 $C_2S = (CaO)_2SiO_2$;
 $C_3A = (CaO)_3Al_2O_3$;
 $C_4AF = (CaO)_4Al_2O_3Fe_2O_3$; $C_4A_3S = (CaO)_4(Al_2O_3)_3SO_3$;
 C-S-H= hydrated calcium silicate ;
 CH : Portlandite ;
 AFM= CaO, Al_2O_3, H_2O sulphated or not)

Our first set of experiment was conducted on synthetic system to avoid the heterogeneity of cement.

Results from the hydration of calcium silicate in presence of low amount of Pb (lower than the $Pb(OH)_2$ precipitation) indicate that Pb induces a hydration hindrance and the formation of C-S-H is delayed. At the end of the hydration process NMR and EXFS showed that Pb and Zn are incorporated in the C-S-H structure at the end of silicate chains (Figure 3). Chromium (III) possesses a high affinity to all silicate and aluminium minerals from cement.

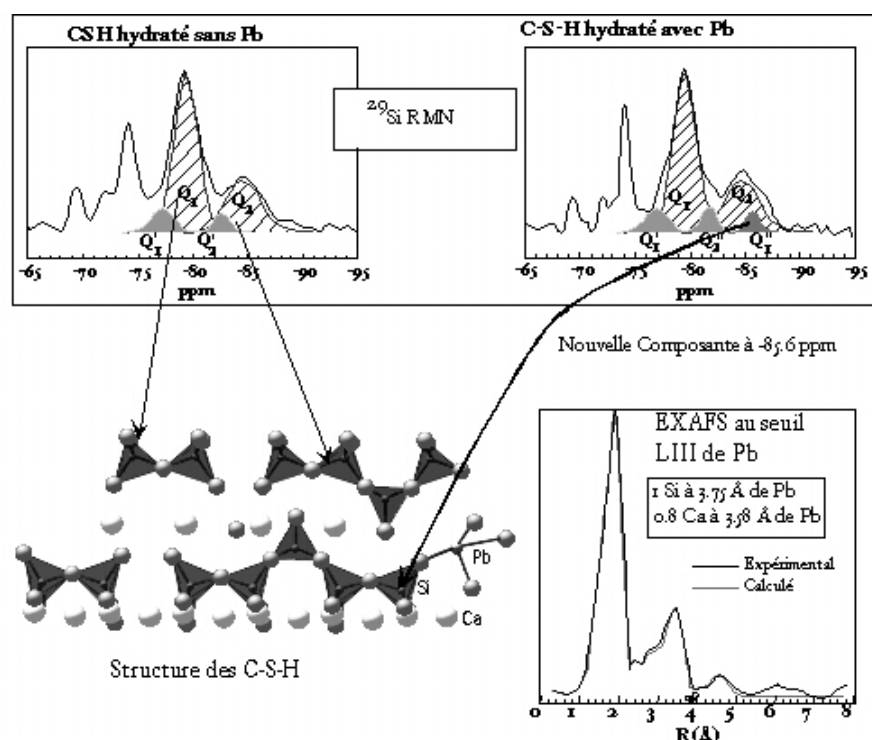


Figure 3: Combination of NMR and EXAFS results to identify the Pb fixation site within C-S-H.

Leaching behaviour of heavy metal in cement.

Following the study concerning the mechanisms of heavy metal fixation by cement phases but on synthetic systems, we have studied the evolution of the heavy metal speciation during leaching of cements. After 40 leaching days at pH=5, 40°C, sample analysis revealed that the altered part of cement can be decomposed in several zones:

- zone Z1 highly porous and composed by amorphous surface phases.
- zone Z2 corresponding to the accumulation of ettringite (1-2 mm from the surface)
- zone Z3 the non altered layer beyond 2.5 mm from the surface.

The evolution of the redox state of chromium was investigated within the altered layer.

The most surprising result concerns the evolution of the Cr(VI)/ Cr(tot) ratio along the line spectra, which is constant from the altered layer to the core (both for doped and undoped samples). This means that the same amounts of Cr- (VI) and Cr(tot) are released during leaching. This result is not in perfect agreement with literature, which usually states that Cr-(VI) is mainly leached out. Although this result must be confirmed, it clearly indicates that Cr(VI) may be less mobile than predicted by models (Figure 4).

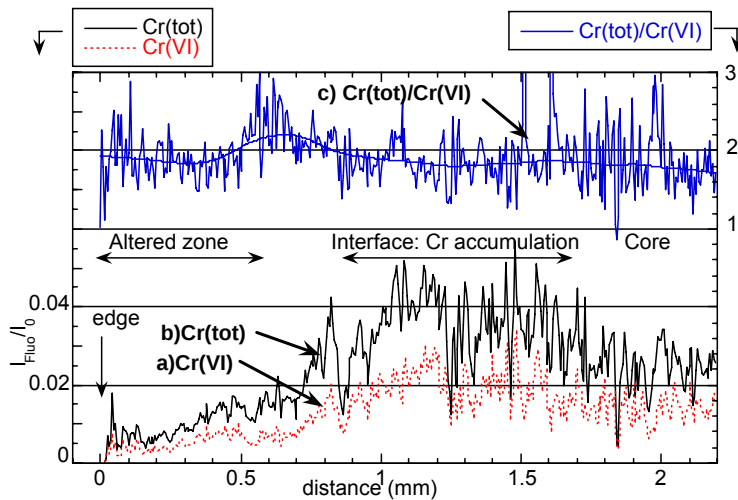


Figure 4: Comparison for one line scan of the $Cr(VI)/Cr(tot)$ values obtained from the line scan with $Cr(VI)$ and $Cr(tot)$ profiles.

We have demonstrated that hydrotalcite can fix Cr in the 0-1 mm zone.

Impact of by-product re-use: case of steel slag.

Basic Oxygen Furnace (BOF) steel slag is obtained during the transformation process of pig iron to steel in LD converters and is attractive as a construction material due to its excellent technical material properties. This by-product is mainly composed of Fe, Ca, Si but also contains trace elements potentially harmful to the environment like Cr and V. Therefore the decision to reuse them should be based on solid knowledge of their environmental impacts particularly from the durability aspect.

The crystal-chemistry analyses of both altered samples indicate that Cr remains at a constant trivalent state, the less toxic and less mobile form, even during leaching. Two Cr-bearing phases have been identified. Initially within unaltered BOF slag, a part of $Cr(III)$ ions structurally replace the $Fe(III)$ octahedral ions in a dicalcium aluminoferrite ($Ca_2Fe_{2-x}Al_xO_5$) and the other part is associated with a solid solution $(Fe, Mn, Mg)O$, close to wustite. The same Cr speciation was observed within the altered regions. However thanks to micro-analysis we have detected high Cr rich regions in the altered layers constituted by a spinel-type phase. The solubility of $Cr(III)$ seems to be partially controlled by this stable phase resulting from $(Fe, Mn, Mg)O$ alteration.

In the case of vanadium results are more contrasting since oxidation of V has been evidenced leading to a significant release of V during lab-leaching tests.

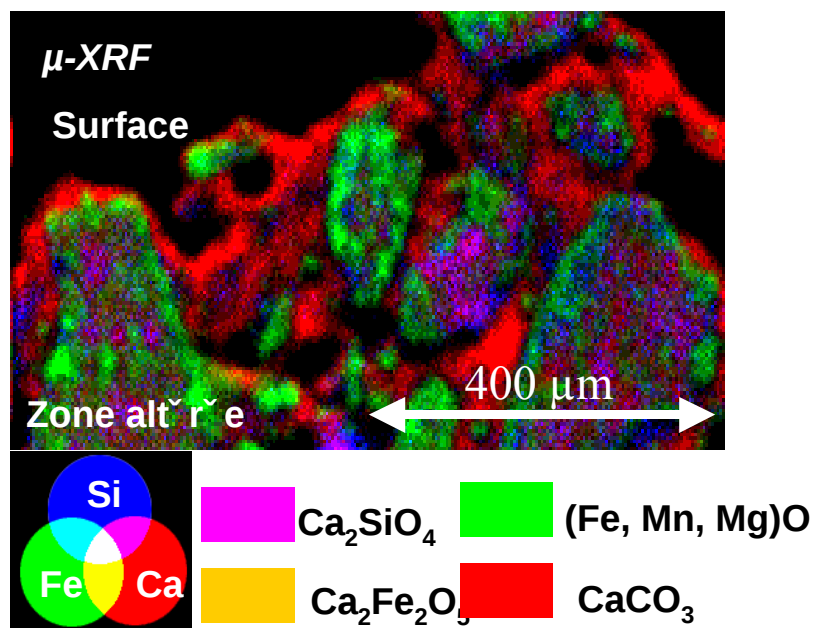


Figure 5: location of new-formed phases after steel slag leaching. (lab micro-XRF data)

Characterisation and modelling geochemical processes controlling the leaching of contaminated materials: a generic approach applied to MSWI bottom ash

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INTRODUCTION

A predictive “multi-surface” reactive transport modelling approach has been developed for the environmental risk assessment of contaminated materials. The approach is based on the identification of the major geochemical processes that control the partitioning of both major and minor elements in the source term, as well as along the transport pathway in soil and groundwater. For this purpose, a combination of consistent leaching/extraction methods and geochemical modelling is used. In this paper the modelling approach is outlined and examples are shown particularly for the case of municipal solid waste incinerator (MSWI) bottom ash.

METHODS

The geochemical part of the model approach incorporates mineral dissolution/precipitation, surface complexation/precipitation on iron- aluminium (hydr)oxides, and complexation with both particulate and dissolved organic carbon, notably humic (HA) and fulvic acids (FA). These reactive organic surfaces have been found to dominate contaminant partitioning in many contaminated materials (e.g. waste, soil, sludges and construction materials) and are, therefore, explicitly considered in the modelling approach. The approach is described in detail in Dijkstra et al. (2006a,b). The major input parameters for the model are the “available” concentrations of the major and trace elements, i.e., the concentrations representing the fraction of these elements that is active in mineral dissolution/precipitation and sorption processes. In addition, the concentrations of the reactive mineral and organic surfaces in the solid phase are input. The methods for the estimation of these parameters have been carefully developed and/or selected, particularly to be consistent with the sorption models used in the modelling approach, and are briefly described below.

A new rapid method has recently been developed to analyse the concentrations of HA, FA and hydrophilic (Hy) acids in both aqueous and solid samples. With this experimental method, the model is parameterised with respect to the concentrations of these humic substances. In addition, a novel approach is used to describe the partitioning of FA based on the surface complexation of FA on iron/aluminium

(hydr)oxides, which allows a “forward” prediction of the FA concentrations in solutions when its total available concentration in the solid phase is known. Amounts of “reactive” iron- and aluminium (hydr)oxides are estimated by selective chemical extraction as described in Dijkstra et al. (2006a). The model further needs parameterisation of the concentrations of major and trace elements that are active in mineral dissolution/precipitation and sorption processes. For waste materials such as MSWI bottom ash, these concentrations are estimated from measurements at pH 2 in the pH static test (L/S 10). Concentrations measured at this pH value generally represent the maximum leached concentrations over the full pH range investigated (pH 2-12). Exceptions are anionic species such as molybdate and FA for which concentrations measured at pH 12 were used, assuming complete desorption at this pH value (for further details see Dijkstra et al. 2006a). For contaminated soils, the “available” contaminant fractions generally require more acid extractions (typically pH = 0.5), as shown in Dijkstra et al. (2004).

The speciation of major and trace elements was calculated with the ORCHESTRA modelling framework (Meeussen 2003), in which the different sorption models described below were implemented. Inorganic speciation and mineral solubility was calculated using thermodynamic data from MINTEQA2 (version 4.0, 1999). Specific and non-specific sorption of protons and ions to FA and HA is modelled with the NICA-Donnan model (Kinniburgh et al., 1999) and “generic” binding parameters as described in Dijkstra et al. (2006a). The Generalized Two Layer Model of Dzombak & Morel (1990) was used to model surface complexation and surface precipitation of ions to Hydrous Ferric Oxide (HFO). In accordance with Meima and Comans (Meima & Comans 1998), amorphous aluminium (hydr)oxides present in the bottom ash matrix were considered as potentially important sorbent minerals, for which HFO was taken as a surrogate sorbent in the model. The model can be applied to both batch and percolation-based leaching regimes, for which the geochemical part is combined in ORCHESTRA with advective/dispersive transport of water and first-order mass transfer between mobile and stagnant zones (dual porosity).

Typical leaching tests that are used for the verification of the predictive modelling approach are the European standardized test methods for waste leaching TS14997 (batch pH-static leaching test, pH 2-12, liquid to solid ratio (L/S) of 10 L/kg) as well as the percolation test TS14405 (natural pH, L/S 0.2 - 10 L/kg). In the latter test, the flow was stopped for 77 hours at L/S ~ 2 and 70 hours at L/S ~ 10, to investigate the effects of non-equilibrium. After the flow interruptions, the percolation was resumed and an “equilibrated” leachate fraction of about 120 mL was collected, which is slightly less than 1 pore volume.

RESULTS

Using a single, independently determined, set of input parameters as described in the Methods section, the generic modelling approach does generally enable adequate model predictions for the leaching of a broad range of major and trace elements from contaminated soils and waste materials, under widely different conditions. In this paper,

results from this approach are illustrated for the case of municipal solid waste incinerator (MSWI) bottom ash. This waste material is produced in very large quantities in many countries, and is often beneficially utilised in construction. The source term of MSWI bottom ash forms a particularly interesting case because of its enrichment in many potential contaminants. In addition, the partitioning between the solid matrix and the leachate of both heavy metals and oxyanions is controlled by both inorganic and organic reactive surfaces. The particular MSWI bottom ash shown in this paper is a freshly quenched sample taken from a Dutch incinerator. This sample has previously been described by Dijkstra et al. (2006a).

Figure 1 shows for fulvic acids and Cu the leached concentrations as a function of pH as measured with the pH-static test and model predictions (top), as well as percolation test results and model predictions (bottom). The leaching of FA is believed to be controlled by sorption of FA to iron- and aluminium (hydr)oxides. The model shown in Figure 1 generally describes the measured pH-dependent leaching of FA adequately, and is based on a new approach using two conditional surface complexation reactions (Dijkstra et al. (2006a). The model prediction for Cu is the result of surface complexation to iron- and aluminium (hydr)oxides in the pH-range 2-6, and precipitation of $\text{Cu}(\text{OH})_2(\text{s})$ toward higher pH. At $\text{pH} > 6$, the leaching of Cu is primarily controlled by the availability and leachability of FA present in the MSWI bottom ash leachates, due to the formation of strong Cu-FA complexes (Dijkstra et al. 2006b).

The bottom diagrams of Figure 1 show that the predicted release of Cu from the columns is strongly determined by complexation to leached humic substances. The model predictions follow closely the predicted release curve of FA. The initial leached concentrations of Cu are predicted adequately, but concentrations during the course of the test are underestimated due to the underestimated leaching of FA. The modelling predictions represented by the grey lines agree much better with the measured leaching of FA and, consequently, Cu and are obtained by assuming (first order) kinetic constraints in the release of FA, as explained in detail by Dijkstra et al., 2006b). Further research is required to establish whether these kinetic features have a chemical (i.e. slow desorption kinetics) or physical nature.

With the model it is possible to investigate the importance of the different solution species as a function of L/S. Figure 2 show calculated speciation diagrams based on the “grey” model scenario (Fig. 1) for Cu. The solution speciation is subdivided into “complexed with FA”, “complexed with HA”, “inorganic complexes” and “free metal” (Me^{2+}). Figure 2 clearly shows that Cu is virtually 100% complexed to leached FA over the full L/S range, confirming the importance of these humic substances in controlling the leaching of Cu (and other heavy metals, see Dijkstra et al. 2006b).

CONCLUSIONS

The “multisurface” reactive transport modelling approach presented in this study enables a strongly improved model prediction and understanding of contaminant source terms, as illustrated here for MSWI bottom ash. Novel aspects of this approach

are the combination of characterisation of DOC in terms of its reactive components (HA and FA), the inclusion of mechanistic models that predict the binding of metals to these substances, the inclusion of a surface complexation model that predicts FA concentrations, and finally, a model that captures the influence of physical non-equilibrium. These features generally enable the model to adequately capture the observed leaching patterns as a function of both pH and L/S for a broad range of major and trace elements. The generally adequate agreement between model predictions and data shows that the use of equilibrium-based geochemical models to dynamic laboratory- leaching tests performed on heterogeneous matrices such as MSWI bottom ash is very promising. Given the dominant effect of fulvic (as well as humic) acids on the leaching of heavy metals, further improvement of the (reactive transport) modelling approach can particularly be achieved by a more mechanistic description of the dynamic leaching behaviour of these humic substances.

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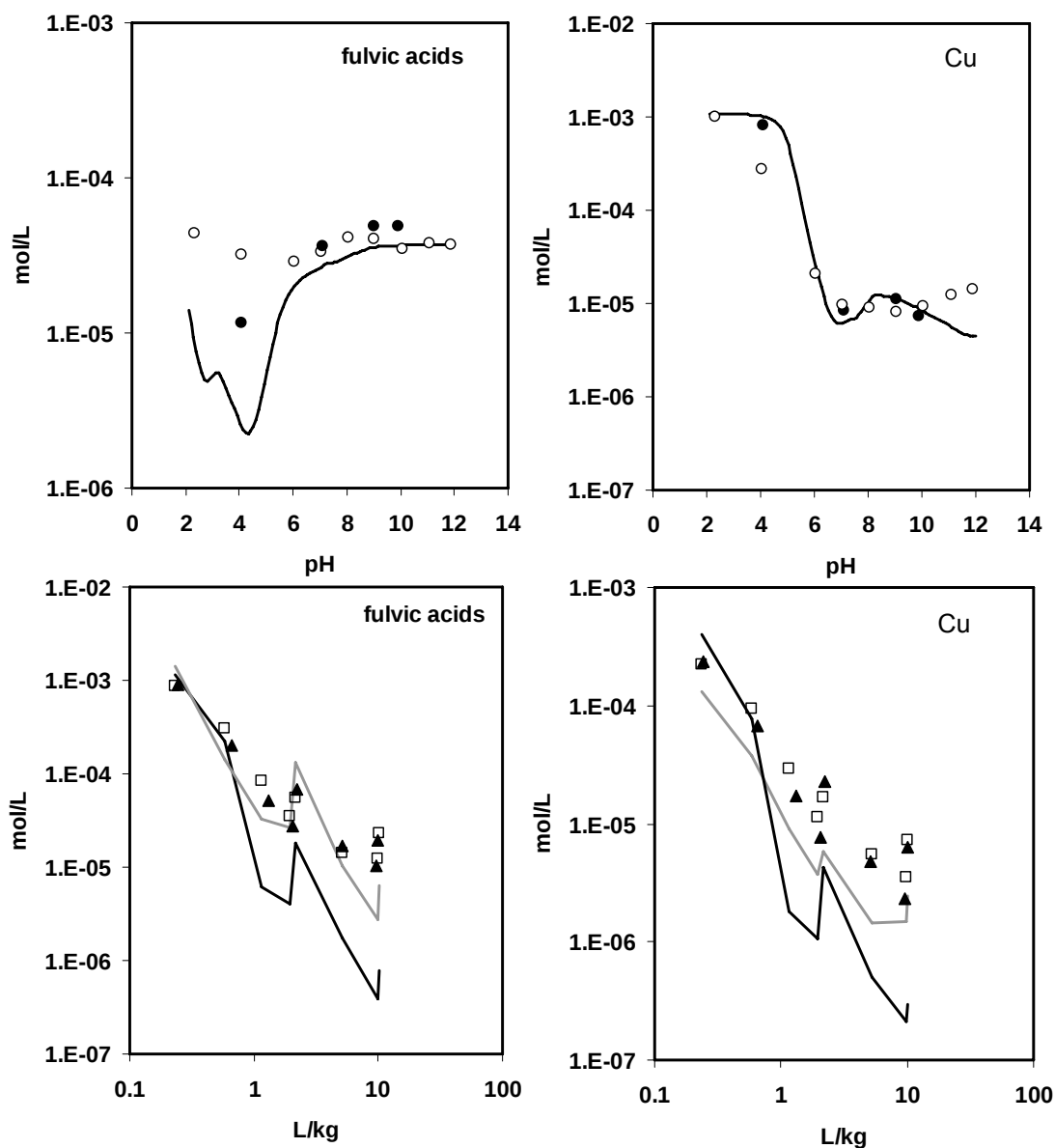


Figure 1. Top: Leached concentrations as a function of pH as measured with the pH-static test (open circles) and model predictions (curves) for fulvic acids and Cu. The closed circles in the diagrams for fulvic acids and Cu are from independent experiments obtained after a longer equilibration time of 168 h. Bottom: Results of the percolation tests and model predictions for fulvic acids and Cu, expressed as a function of cumulative liquid-to-solid ratio (L/kg). Open squares are the data collected at the flow velocity prescribed by TS14405 (CEN, 2004), closed triangles are the data collected at a four times faster flow velocity. Fractions at ~ L/S 2.2 and L/S 10 were collected immediately after flow interruption. The solid lines represent model predictions by the reactive transport model. The grey lines are model predictions calculated for each data point separately. See Dijkstra et al. (2006b) for further details.

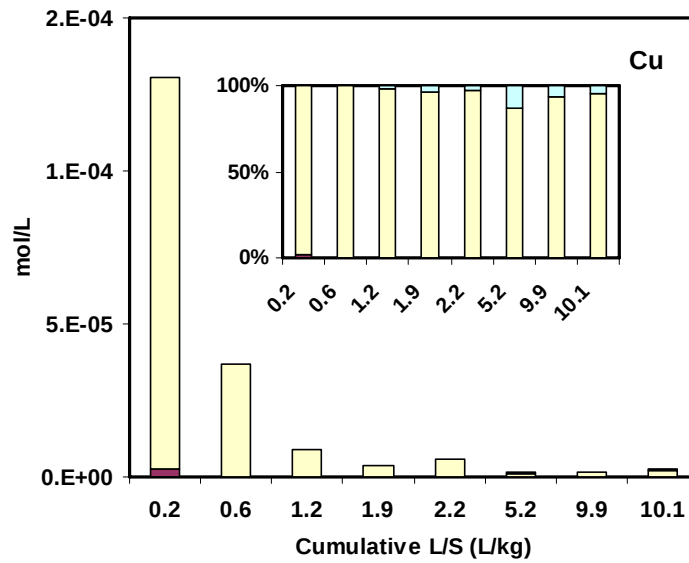


Figure 2. Solution speciation of Cu among the different surfaces considered in the model. 'DOM-FA' = bound to fulvic acids (yellow), 'DOM-HA' = bound to humic acids (purple), 'Inorg' = inorganic complexes such as Cl and OH species (light blue), 'Free' = free ions (Me^{2+}) (white). The figure complements the predicted concentrations based on the model scenario indicated by the grey curves in Figure 1. See Dijkstra et al. (2006b) for further details.

pH dependence test interpretation throughout mineral dissolution/precipitation processes

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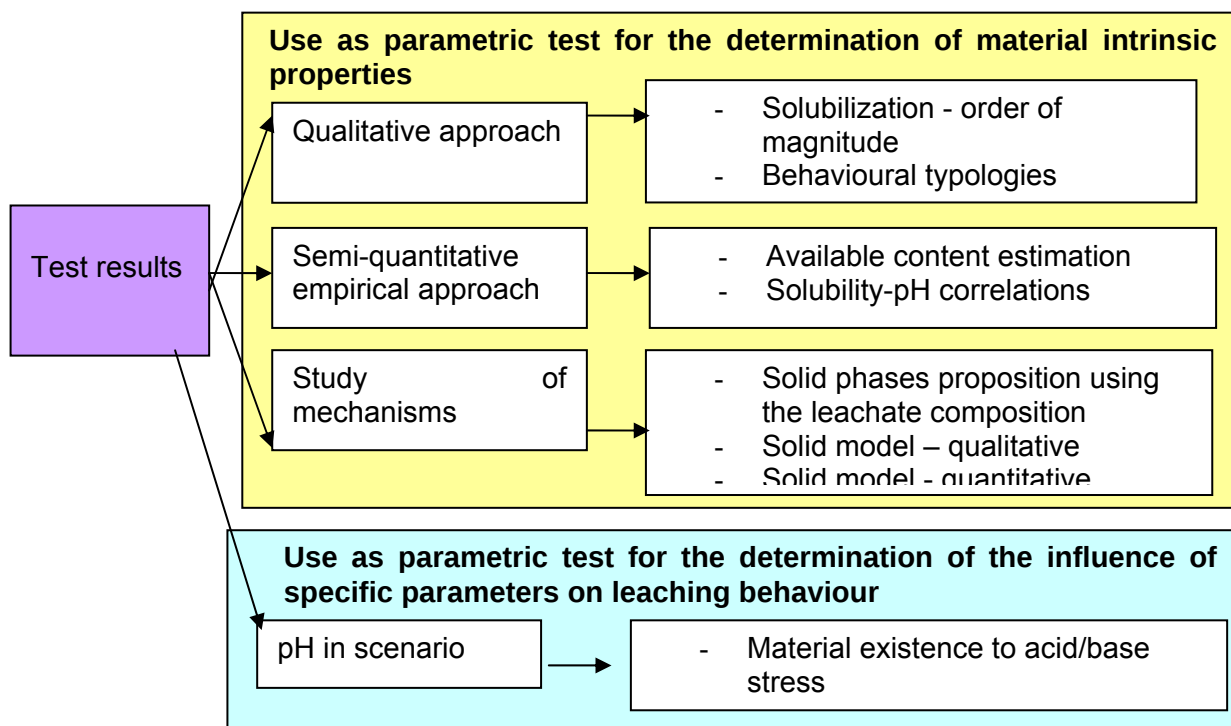
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Abstract

The pH dependence test known in two versions, i.e. pHstat and ANC, is more and more used for geochemical modelling proposes. The literature survey revealed a broad variety of interpretation approaches, no reference or modelling guide being available at present. Some aspects of the test results use for geochemical modelling are discussed here: the equilibrium state and the time scale of experiments and modelling objectives, the qualitative and quantitative modelling of the solid/liquid system, and validation possible approaches. An example of geochemical modelling methodology is detailed for the case of coal fly ashes.

Introduction

A bibliographic survey revealed several ways of using the pH dependence test results (presented in figure 1) as well as a current tendency towards the quantitative modelling approaches. The ANC or pHstat tests are more and more used for modelling proposes, especially for geochemical modelling. Some aspects of the geochemical modelling methodology and its application are presented here aiming to reveal several key problems.



Some principles reminder

Equilibrium state. The pH dependent test is traditionally an equilibrium assay.

How to appreciate an equilibrium state? Equilibrium or pseudo-equilibrium? The response needs specific experiments (e.g. kinetic study) and depends on the nature of the material.

Equilibrium laws. One of the equilibrium laws is the phase rule establishing the maximum number of phases existing in a system at equilibrium. For a water/solid system at constant T and P, it can be demonstrated that the maximum number of solid phases equals the number of chemical elements except H and O.

Stability of solid phases. For a solid behaving as different structures:

The more soluble “active” form (microcristalline, amorphous, disordered lattice) is obtained in laboratory conditions (short-term), and in strong oversaturated solution.

The less soluble “inactive” form (crystalline or amorphous) is obtained in natural conditions, at long term, and/or slight supersaturation.

The “active” form transforms on “inactive” under long time (geological), that is the ageing of the solid.

Precipitation kinetics. The first step is the nucleation characterised by the kinetic equation:

$r_N = A \exp(-\Delta G^*/kT)$ where A is the collision efficiency and ΔG^* the activation barrier depending on the interfacial energy. Consequences:

- 1) *The probability to precipitate a given phase depends on temperature.* A typical example is the case of high temperature solids (like melilites) which can not precipitate at normal T even if for the precipitation reaction $\Delta G < 0$, i.e. the reaction is possible from a thermodynamic point of view!
- 2) *The precipitation priority rule of Ostwald:* the precipitate with highest solubility will form first in a consecutive precipitation reactions. The precipitation of the more soluble form is kinetically favoured, e.g. the amorphous form of a hydroxide precipitates before the crystalline form.

Examples of rapid precipitations: hydroxides, sulfides. Very slow precipitations: for dolomite the solubility equilibrium (precipitation) time is unknown!

Dissolution kinetics. The rate of dissolution is controlled by several processes:

- 1) *The mass transfer:* - in fluid phase – rapid processes, depends on : temperature, particle diameter, viscosity, local fluid velocity, diffusion coefficient in liquid;

- 2) in solid phase – slow process, depends on diffusion coefficient in the solid, on temperature.
- 3) *The surface chemistry*: slow process, depends on the chemistry of the surface and the liquid composition. Controls the most important dissolution reactions, e.g. oxides, silicates. (For example, for a silicate crystal only a few monomolecular layers are dissolved/year.)

In natural systems rapid dissolution is considered for: calcareous rocks, sulphates, halides, while slow dissolution: quartz, silicates –possible weathering to gibbsite, kaolinite, smectites, illites. The dissolution mechanism depends also on external conditions. Ex. CaCO_3 : pH acid – “instantaneous”, limited by transfer in liquid phase. pH neutral and basic – surface controlled dissolution.

Remarks: The time scale taken into account for modelling or forecasting is the most important parameter. The equilibrium state in a thermodynamic sense is an ideal state, very likely never reach in real cases. More realistic is to speak about pseudo-equilibrium states for a given time scale – this reveals the necessity to acquire knowledge on dissolution and precipitation rates!

Example of geochemical modelling using ANC test results

The objective of the geochemical modelling is to build a solid model for the material and a reactivity model for the material/water system, for a *given time scale*. The modelling methodology is presented through an example taken from our last studies and concerning the leaching of a coal fly ashes.

Elementary total content. Total content is necessary to perform mass balance calculations and sometimes for the available content estimation for soluble elements.

The pseudo-equilibrium state in laboratory conditions. Before performing the ANC test, a kinetic study is necessary in order to evaluate the pseudo-equilibrium state. In the experimental conditions characterized by a first contact of the material with water, a closed isolated system and a short time scale, the system was supposed at steady state after 10 days. These results do not exclude the possibility of ongoing slow dissolution reactions.

Mineralogical composition. The major phases are easily detected by X-ray analysis. In this example: Quartz (SiO_2), Mullite ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$) and Periclase (MgO). Additional information about the mineralogy comes from literature survey ([2]-[8]) on the composition of fly ashes. The following crystalline phases have been found by different authors: Hematite (Fe_2O_3), Magnetite (Fe_3O_4), K-feldspar (KAlSi_3O_8) and Na-feldspar ($\text{NaAlSi}_3\text{O}_8$), Lime (CaO), Anhydrite (CaSO_4), Gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), Akermanite ($2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), Anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), Calcium-aluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$), Tricalcium-aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$).

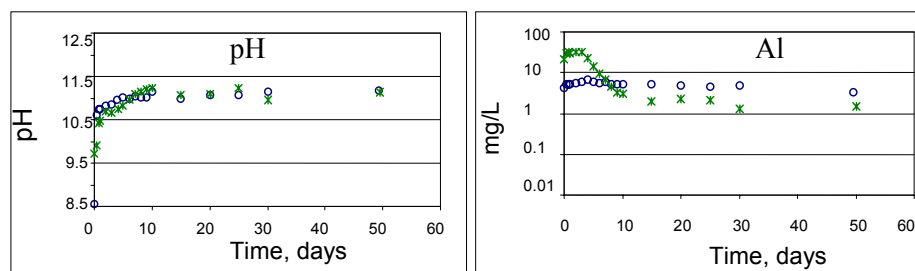


Figure 1. Dissolution kinetics [1]

Legend :
 ○ L/S=10 mL/g
 * L/S=1 mL/g

Secondary minerals can be obtained after hydration of ashes, among these minerals can be quoted: Portlandite ($\text{Ca}(\text{OH})_2$), Calcite (CaCO_3), Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), Brucite ($\text{Mg}(\text{OH})_2$).

Concerning the trace elements only few data exist. The leaching of Cr (VI) can be due to BaCrO_4 and $\text{Ba}(\text{S, Cr})\text{O}_4$ which is a solid solution with different S/Cr proportions. $\text{Ba}_3(\text{AsO}_4)_2$ is the phase suggested controlling the solubility of As(V). Powellite (CaMoO_4) appeared to control the Mo concentration and MoO_4^{2-} forms complexes on iron hydroxide surface. The control of the As, Mo, V, Cr concentrations was supposed to be due to adsorption/desorption reactions on iron oxides and alumino-silicates. The leaching of Ba and Sr from fly ash can be controlled by a solid solution $(\text{Ba, Sr})\text{SO}_4$. In conclusion, it is expected that Ba^{2+} , Sr^{2+} , CrO_4^{2-} and SO_4^{2-} exist as complex solid solutions in the fly ash or neo-form solid solutions further to contact with water.

Use of ANC data

1) *Use of leachate composition for a preliminary calculation.* The plateau of composition observed after 10 days contact is used hereafter. The nature of certain solid phases, i.e. phases controlling the solubility and if the concentration corresponds (or is close) to the solubility value, can be identified from the saturation indexes SI calculated for the experimental composition of the solution. The SI calculation indicated the following phases (in the limits of the used data base) being in a near equilibrium state with the leachate: Brucite ($\text{Mg}(\text{OH})_2$) $\text{SI} = -0.5$, Gibbsite ($\text{Al}(\text{OH})_3(\text{c})$) $\text{SI} = 0.01$, Barite (BaSO_4) $\text{SI} = 0.3$, $\text{BaHAsO}_4 \cdot \text{H}_2\text{O}$ $\text{SI} = 0.08$, CaMoO_4 $\text{SI} = -0.9$.

2) *Building of a rough solid model* using all information on its mineralogy.

Na, K and Cl are supposed to come from soluble phases like Halite (NaCl) and Sylvite (KCl) (concentrations are independent of pH, the concentration of Cl was of the same order of magnitude as the Na and K concentration).

A reactive hydrated calcium silicate as Okenite ($\text{CaSi}_2\text{O}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$) is necessary in the model to account for the buffer capacity of the material (see below). At the natural pH of the material (10.7) the Calcite (CaCO_3) is stable and very likely to occur.

A soluble fraction coming from a small quantity of Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) completely dissolved can explain the pH-independent concentration of SO_4^{2-} .

The elemental analysis of the waste points out that only a small fraction of Cr exists in (VI) valence state, the major quantity behaves as Cr(III) oxides with a very low solubility. The Cr(VI) solid fraction seems to be responsible of the chromium dissolution by leaching. A relatively soluble phase, BaCrO_4 , was considered.

Arsenic behaves mostly as arsenates AsO_4^{3-} in the redox context of the waste in contact with atmospheric oxygen. $\text{BaHAsO}_4 \cdot \text{H}_2\text{O}$ and CaMoO_4 were retained for As and Mo speciation in a chemical environment characterised by a basic pH. However, in the material and before the contact with water they can also occur as surface complexes with the ferric hydroxide or other active surfaces.

Concerning Barite (BaSO_4), simulations performed in different conditions corresponding to complementary leaching tests (percolation) showed that the more suitable is to consider a solid solution containing Ba^{2+} , Sr^{2+} , SO_4^{2-} and CrO_4^{2-} instead Barite.

3) *Neoformations and kinetics*. The simulation of all the test samples (pH varying from 3 to 12) in which acid or base was added permitted to fit the mineralogical model and to semi-quantify the solid phases.

- -Some solid phases can dissolve but not precipitate: case of high temperature formed silicates, stable phases with low rate precipitation like oxides.
- -In the case of metals susceptible to precipitate as hydroxides in the experimental conditions, the most soluble hydroxide was chosen.
- -A surface complexation model (diffuse layer, Ferrihydrite, [9]) was added in order to explain the behaviour of As, Cr and Mo at neutral and acidic pH.

4) *Quantitative modelling*

Ca-containing phases were quantified by fitting the model to the ANC (pH – mmol H+) curve and to the Ca concentration-pH curve. The Periclase (MgO) detected in the material hydrates to Brucite ($\text{Mg}(\text{OH})_2$); its quantity was fitted to the Mg concentration-pH curve (corresponding to the maximum Mg concentration). The Gibbsite quantity can be estimated by fitting to the ANC curve in the pH=4 zone. Gypsum quantity was estimated from the sulphate concentration.

The maximum quantity of As and Mo dissolved in the ANC test was considered to estimate the solid phase quantity. The quantity of ferric hydroxide was adjusted to obtain the best concentration simulations for Cr, As and Mo.

Table 1: Solid phases and fraction of element total content considered in the model [1]

Solid phases :	mmol/kg fly ash	Element	% of TC
BaCrO4	0.05	Al	0.6
BaHAsO4.H2O	0.7	As	104.9
Periclase (MgO) or Brucite (Mg(OH) ₂)	13	Ba	80.7
Calcite (CaCO ₃)	40	Ca	65.5
CaMoO ₄	0.018	Cr	1.4
Ferrihydrite (Fe(OH) ₃)	0.6	Cr VI	104.0
Gibbsite (Al(OH) ₃ (c))	5	Fe	3.0
Gypsum (CaSO ₄ .2H ₂ O)	10	K	2.9
Halite (NaCl)	2	Mg	3.1
Okenite (CaSi ₂ O ₄ (OH) ₂ .H ₂ O)	20	Mo	18.8
Portlandite (Ca(OH) ₂)	9	Na	4.2
Solid solution (BaSr)(CrS)O ₄	20	S	100.0
Sylvite (KCl)	2.4	Si	6.4
Al(OH) ₃ (a)	neo-formation	Sr	100.7
SiO ₂ (a)	neo-formation		
Kinetic reactants	mmol/kg fly ash	parameter	
Albite (NaAlSi ₃ O ₈)	23.8	$p_1=5.10^4$	
K-feldspar (KAlSi ₃ O ₈)	238	$p_1=1.10^6$	
Ca-Olivine (Ca ₂ SiO ₄)	4.7	$p_1k_r=2.10^{-5}$	

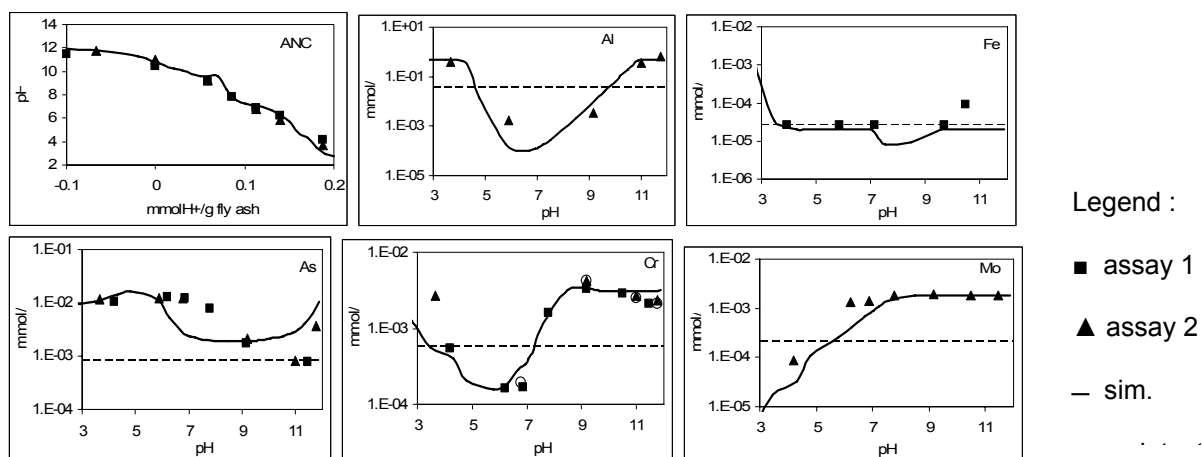


Figure 2: Experimental and geochemical simulation results for the ANC test [1]

Validation and improvement

An additional leaching test was used to validate the model. The simulation of a percolation column revealed some shortcomings. The model was improved for pH, Na, K, Ca at more long term leaching by introducing kinetic reactants, and for an observed correlation between Ba, Cr, As, S by considering a solid solution.

A mass balance of the system was performed (see table 1). The quantity of several elements like As, Cr(VI), S, Sr taken into account in the model represents 100% of the element total content in the fly ash. The other elements exist also as very low soluble (and/or very slow dissolution) phases which can not be identified by this methodology.

The model was further applied in a more complex situation: the leaching under natural conditions of a field pilot (for more details see [1]).

Conclusions

Some specific aspects of the test results use for geochemical modelling are highlighted below.

Only reactive phases are “visible” experimentally. This implies for the modelling:

- the definition of the time scale for the experiments and modelling;
- the selection of phases the chemical properties (kinetics, stability) are in agreement with the time scale.

Quantitative aspects – specific contribution of the test:

- 1) The neutralisation curve (pH versus H⁺ added) – useful data for the quantitative determination of acid/base buffering phases;
- 2) pH conditions for the complete dissolution of some solid phases – quantification of these phases (elements available quantities).
- 3) Identification and quantification of minor phases containing trace elements.
- 4) Identification of specific chemical mechanisms like the surface complexation but also the interactions with soluble organic mater.
- 5) The leachate composition and pH serve as fitting parameters for the model

The most soluble phases control the leachates’ composition and are then “visible” by the ANC test results. Consequently a model based only on these results is partial. Its use for long term forecasting requires complementary knowledge on the solid mineralogy and reactivity.

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How uncertain can geochemical and hydrological information be for the long-term prediction of contaminant leachability from ashes and cementitious materials

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Abstract

The release of contaminants to the environment is one of the major concerns in the management of wastes, either for reuse or landfilling. The last decade has seen great strides in our understanding of leaching processes and the information gained is being used in the development of European policies in the management of waste materials. We understand the main geochemical and hydrological factors that control heavy metal and metalloid leachability. In the normal evolution of research activities aimed at understanding environmental phenomena, we have reached a point where we need to take stock. From a very superficial test-based approach to leaching assessment very detailed models have been developed. Do we know enough to be able to advise legislators and above all practioners on practices in the landfilling or reuse of secondary materials? This workshop provides an ideal opportunity for exchanging ideas on this topic.

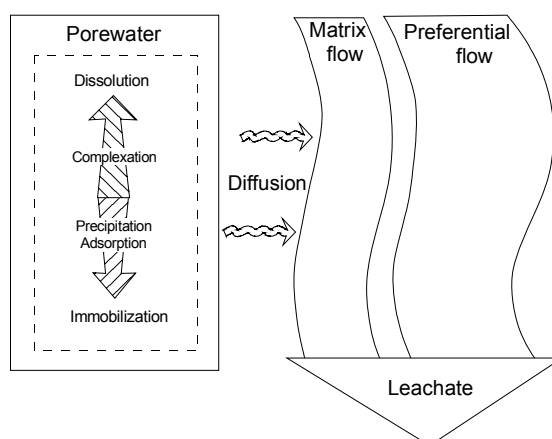


Figure 1: Essential components of the leaching process

Figure 1 shows the essential processes involved in the leaching process, namely

- ***Geochemical factors within the porewater***

Our understanding of the geochemical processes in alkaline media has expanded greatly within the last decade, making use of the current understanding of cement chemistry. Most likely one of the greatest uncertainties remains the binding mechanisms in relation to cement minerals. Also, the products and solubilities of metals and metalloid species as a result of carbonation have been addressed in recent years.

- ***Diffusion processes within the solid matrix***

Diffusion processes, particularly with matrix changes are particularly difficult to determine

- ***The hydrological regime within a particular use or landfill scenario***

There are a number of in-depth studies of landfills, lysimeters and road bases that have addressed this problem

This talk addresses the uncertainties associated with modelling long-term leaching behaviour in relation to the time frame that we require to understand.

Present state and perspectives of reactive transport modelling for risk assessment and leaching tests

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Abstract

Reactive transport models have proven to be highly effective tools to better understand the behaviour of bio-geo-chemically reactive systems subject to hydrodynamic processes, via a wide variety of applications in different domains and at different scales. The simulation of leaching tests and, ultimately, the prediction of the behaviour of similar systems at larger scales typically requires the reactive transport modelling approach. Generally, both geochemical and hydrodynamic facets are tightly linked together and a strongly coupled modelling approach is required, solving the equations involved in bio-geo-chemistry and in hydrodynamics simultaneously. Here we propose to focus on the description of reactive transport models, emphasizing the conceptual and numerical implementation of features and processes important for leaching of mineral wastes.

Introduction

Reactive transport models combine microbiological and/or geo-chemical reactions with hydrodynamic processes such as water flow, diffusion and dispersion. They are increasingly used in risk assessment to understand and to predict the behaviour of reactive phases in natural or engineered systems [1]. Recently, reactive transport models have proven to be useful tools in the field of solid waste management and leaching processes in general. Leaching of solid waste forms such as *bottom ashes* in road constructions is generally adequately modelled by only a few key-processes. A model based on Brownian motion (diffusion) and simple chemistry (precipitation and/or dissolution) is indeed often sufficient to correctly model experimental results. This permits the use of a simplified *ad hoc* code [2].

Another option is to use a more general-purpose reactive transport model. Chemical reactions are considered since they affect the mobility of chemicals: retention by matrix-forming minerals, precipitation and dissolution reactions are straightforward examples. Chemistry also indirectly contributes to the migration behaviour via complexation by mobile substances (organics, colloids) and local pH and ionic strength conditions. In turn transport conditions may be altered by chemical reactions: dissolution of mineral phases may increase the porosity or lead to exposure of new mineral phases to the aqueous solution. On the other hand, precipitation may lead to clogging of part of the pore space and therefore reducing the diffusion coefficient and permeability of the medium. This feedback mechanism is particularly important at very reactive interfaces such as are found between cement and clays [3].

A major advantage of the latter option is that modelling concepts and the associated database are readily transposed to other scales, with possibly more complex boundary conditions and additional chemistry to deal with. As the same model can deal with batch-, flow-through and column experiments, we preserve internal consistency and avoid error-prone transcription of data between intrinsically different codes. This is even more pertinent when moving from laboratory to field scales. For example, *in situ* conditions may require an unsaturated flow model or a meteoric upper boundary condition: the physico-chemical processes retained to simulate the leaching process in laboratory conditions still remains valid and can be used under non-saturated conditions – provided, of course, that this option is properly and consistently implemented.

The drawback of using fully fetched reactive transport models is that, in an attempt to correctly describe a large number of simultaneously occurring processes, they tend to become increasingly complex. Consequently, verification and validation of the codes becomes an issue of concern. Moreover, their use in decision-making and critical or sensitive application domains require a rigorous and permanent verification and confidence-building process. The development of HYTEC, for example, is governed by a French national consortium, which guards against non-regression and guides the development in function of industrial and scientific needs.

Reactive transport models are often evolutions of either a hydrodynamic transport model (enriched with chemical processes) or a bio-geo-chemical code (enriched with hydrodynamic processes). Examples of the first class of models are SHEMAT [4], MCOTAC [5] and RT3D [6]. Examples of the second class are e.g. PHREEQC [7] and PHAST [8]. Some codes are developed *from scratch* for coupling purposes: HYTEC [9], ORCHESTRA [10] and CRUNCH [11] are only a few examples of recent instances. They all deal with the major features and processes involved in chemistry and hydrology, but differ in specific options, databases, precision and numerical solution methods – not to mention the user interface (ease of use). Therefore, the choice of reactive transport model will depend on the application domain of interest.

Important features and processes

Reactive mass transport in a porous medium is generally modelled by the usual form of the advection/dispersion equation:

$$\frac{\partial(\vartheta C_j)}{\partial t} + \frac{\partial(\vartheta \bar{C}_j)}{\partial t} = \nabla \cdot (D \nabla C_j - U C_j) + q(C_j)$$

where ϑ denotes the water-content of the medium, C is the mobile and $\bar{C}$ the immobile concentration of species j , such that the total concentration is $\bar{C} + C$. D includes diffusion and dispersion and U is the filter flow vector. The right-most term represents a local, flow-independent source or sink. Assuming laminar, isothermal and incompressible flow in porous media, the velocity field is obtained by Richard's equation that, under saturated conditions, reduces to the well-known equation proposed by Darcy with ϑ being equal to the porosity of the medium. This equation is readily solved using appropriate numerical techniques. For multi-component reactive

transport, the finite-volumes approach has some interesting advantages with respect to e.g. finite elements or differences [9].

Bio-geo-chemistry defines which fraction of an element is mobile or immobile. If, for example, we consider a medium which contains lead, the mobile fraction is the sum of all ionic Pb species (Pb^{2+} , PbOH^+ , $\text{PbCO}_3(\text{aq})$,...) and the immobile fraction is the sum of all mineral Pb species (cerussite, litharge,...) plus the sorbed fraction, if processes like surface complexation and cation exchange are involved. A speciation model is required to precisely establish the immobile fraction, but also provides other useful information: e.g. some aqueous complexes are more bio-available than others and therefore more relevant for risk assessment.

Often, $\bar{C}$ is calculated using a simple linear relationship, $\bar{C} = K_d C$, with K_d being the distribution coefficient. Within the transport equation, the K_d leads to a linear retardation-coefficient, applied to the diffusion, dispersion and advection terms. This approach should be used with care for the following reasons:

- the fundamental principle of mass conservation is not respected: the total amount of species C_j is not fixed but a function of the mobile fraction;
- the distribution coefficient lumps a certain number of system parameters which are not constant when scaling up. Among others, the value of K_d depends on the water-exposed surface area and solid/liquid ratio, which change significantly when moving from unconsolidated matter to porous or fractured media;
- variable chemical conditions have a sometimes significant impact on the distribution coefficient, due to e.g. aqueous complexation, competition effects and redox processes [1].

Instead, $\bar{C}$ should be evaluated by an approach based on phenomenological processes, possibly surface complexation and/or cation exchange, and appropriate models accounting for e.g. electrostatic effects, Donnan potentials and water-accessible surface areas. This approach may require parameter values that are not necessarily provided by the available experimental data. Recent thermodynamic databases, however, provide reasonable estimates for many parameters. Others need to be estimated, which introduces the notion of uncertainty – only rarely taken into account in risk assessment studies but feasible and necessary.

Kinetics add another level of complexity to reactive transport models. Most experiments require a kinetic approach to correctly simulate mobilisation of metals due to dissolution. A simplification to account for kinetic inhibition of the expected thermodynamic equilibrium is to reduce the thermodynamic formation constant of the solid phase [2]. This may lead to an acceptable fit of the experimental data but introduces the risk of underestimating the mobile fraction if the database is used in another context or at larger time scales – e.g. *in situ*. Moreover, kinetics are the basis of modelling microbial processes. Using a trustworthy thermodynamic database in combination with a plausible kinetic inhibition process is expected to perform much better at different timescales.

A propos: the HYTEC model

HYTEC is a reactive transport model integrating a wide variety of features and options, which, after a decade of development, has evolved to a versatile simulation tool [9]. Bio-geo-chemistry is provided by the module CHESS. Accordingly, the model accounts for many commonly encountered processes including interface reactions (surface complexation with electrostatic correction, cation exchange), precipitation and dissolution of solid phases (minerals, colloids), organic complexation, redox and microbial reactions, etc. All reactions can be modelled using a full equilibrium, full kinetic or mixed equilibrium-kinetic approach. Thermodynamic data is taken from the database developed by the Common Thermodynamic Database Project (CTDP) [12].

The hydrodynamic module of HYTEC is adapted for hydrodynamic conditions commonly encountered in the laboratory or in the field. Among others, the code allows for unsaturated media, variable boundary conditions, sinks- and sources. HYTEC searches for an accurate solution to the multi-component transport problem using an iterative, sequential, so-called *strong coupling scheme*. Strong coupling permits variable hydrodynamic parameters in function of the local chemistry. For example, the porosity of a porous medium reduces after massive precipitation of neo-formed mineral phases, which modifies the water flow paths and transport parameters, e.g. diffusion coefficients: HYTEC solves this interdependency accurately, which makes the tool particularly useful for e.g. cement alteration at long timescales (e.g. storage of waste and performance assessment).

The application domains and scales of HYTEC are numerous, as illustrated by Figure 1. Simulation of cement hydration requires extremely short space (and time-) scales. Degradation of materials such as ashes, concrete and cement generally implies a modelling unit at intermediate scales, typically in the order of a litre. Waste dumps, (e.g. mine tailings), deep underground radioactive waste disposals and sequestration of green house gases are simulated at much larger time and space scales, as illustrated by the figure.

Recent research with HYTEC is focused on the long-term stability of cement and concrete. Concrete is often simulated by a typical CEM-I cement including mainly portlandite, CSH.

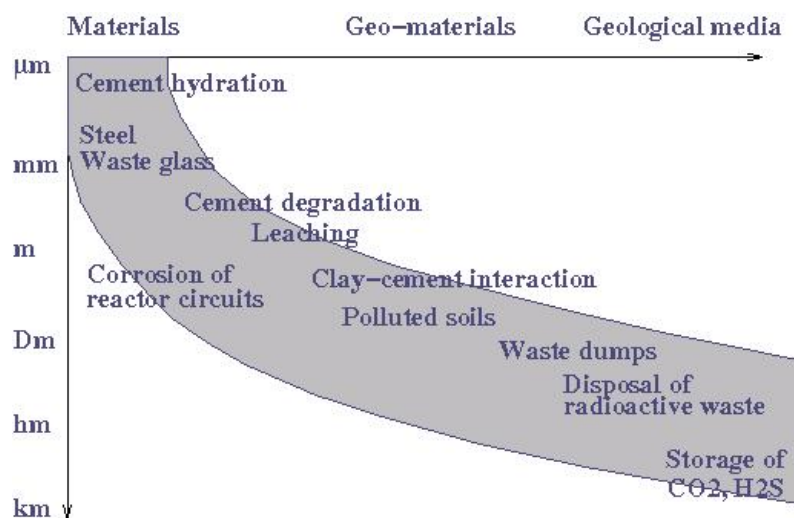


Figure 1. Application domains of the reactive transport model HYTEC. Most applications are carried out within the framework of the Reactive Transport Consortium PGT.

(calcium-silicate hydrate with a high Ca/Si ratio) and small concentrations of ettringite and calcium monosulfo-aluminate. More sophisticated models for cements are sometimes used, including sorption on primary or secondary CSH phases, carbonation and sulfatation of the material. These features, as well as the strong coupling approach as outlined above make HYTEC particularly useful for the modelling of long-term leaching of solidified wastes [13].

Conclusion and perspectives

Risk assessment, waste management and fundamental scientific research require a modelling approach, which covers all scales involved. Today's reactive transport models provide a solution to this problem, allowing to simulating numerous, sometimes tightly interweaved processes in an accurate manner. They become predictive tools, applicable to long-term dynamic leaching of wastes, to performance or risk assessment of waste repositories and to related application domains.

Although the application of simplified models is seemingly justified by good fits to experimental data, they contain the potential danger of wrongly predict the system behaviour at larger scales. For example, replacing kinetic inhibition by lowering the thermodynamic formation constant of the waste matrix may lead to an underestimation of contamination if extrapolated to larger time scales. Similarly, K_d coefficients should be used with care or avoided if possible. Instead of simplifying the system, it is preferable to use a fully fetched reactive transport model, even if the latter requires more parameters than actually obtainable by the experimental data: in that case, they can be estimated. Unknown or estimated parameters values are useful since they allow us to quantify, to some extend, the uncertainty involved in the simulations.

With respect to uncertainty, thermodynamic database development remains one of the key issues of the reactive transport problem. The increase in the use of chemical models and the tremendous amount of work involved in developing and maintaining an operational thermodynamic database require new methods, based on collaborative efforts of the international scientific community. Databases should not only contain thermodynamic values, but uncertainty estimates as well. Also, further progress is required on the topic of sorption processes (sorption databases), kinetic data, the role of colloids in natural systems and microbial activity, the latter playing an important role in virtually all subsurface systems.

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MODELS FOR IMPACT EVALUATION ON EARTH CONSTRUCTIONS AND LANDFILLS –ASPECTS FOR APPROPRIATE MODELLING

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Background

Information on tools and models suitable for the prediction of the leaching of compounds from waste and by-products together with the transport of leached compounds to the environment was discussed in a Nordic project “Models for impact evaluation on landfill – aspects for appropriate modelling” (2004-2005) financed by Nordic Innovation Centre and carried out by VTT in cooperation with its Danish partner DHI and Swedish partner SGI. The project also focused on the purpose and outcome of some models suitable for release prediction from wastes and contaminated soils. Moreover, key parameters needed as input data in the modelling and examples of modelling results are presented. The aim was also to raise the interest for the use of modelling for decision making and to highlight aspects important for proper modelling.

Modelling and its results are important tools for evaluations of environmental risks. However, currently limited attention has been paid on quality aspects and transparency of modelling work. For example requirements for proper modelling are often lacking. The understanding of relevant input data and possible outcome from modelling enables the end-user and also the authorities to bring up the key questions to be answered by modelling and through that also help the modeller to focus on the relevant modelling tasks. This paper highlights aspects important for end-users.

Drivers and goals for modelling from waste materials

The Council Decision 2003/33/EC on waste acceptance criteria related to the EU landfill directive 1999/31/EC gives acceptance criteria for wastes (primarily limit values for the leaching of predominantly inorganic compounds) to be disposed of at landfills for inert waste and hazardous wastes and also for stable, non-reactive hazardous waste to be placed in non-hazardous waste landfills (and for non-hazardous waste to be placed in the same cells). Criteria for the other types of landfills and for contaminants not included in the EU regulations are to be developed on a national basis.

The Council Decision allows member states the possibility on a case-by-case basis, to allow up to three times higher limit values for specific wastes and specific compounds. However, the use of higher limit values requires a risk assessment to demonstrate that there will be no additional risk to the environment. The requirements for the landfill

construction and leachate collection can also be reduced on the basis of an assessment of environmental risks. It has then to be shown that the landfill poses no potential hazard to soil, groundwater or surface water. The same kind of impact evaluation is also needed for wastes to be landfilled, where national criteria may be set for contaminants that are not included in the EU regulation.

Same kind of impact evaluation is also needed for industrial by-products, construction materials and wastes used in earth construction. Especially in cases when limit values are exceeding or materials are not within the scope of specific regulations, the impact evaluation offer the possibilities for demonstrating acceptable risks from utilisation in earth construction.

Typical end-users of waste modelling results are scientists, legislators, authorities, waste producers and landfill operators. The end-user usually needs information from the modelling for the assessment of the impact from waste on water quality in different scenarios. This information makes comparisons of management options possible. Here both variations with time and disposal conditions at different points of compliance are needed as well as total load. The impact evaluation is usually done by comparing estimated concentrations and fluxes to criteria or reference points of interest, e.g. background concentrations (sea water, surface water), drinking water, or other criteria given for protection of aquatic life.

General requirements for appropriate modelling

In the Nordic project it was concluded that the modelling work is best described in terms of a series of consecutive steps. Especially the information needed and the expected outcome from each step was discussed and is listed Table 1.

The following general requirements were regarded important to be addressed in modelling work:

- a qualitative systematic description of the landfill and groundwater system and the design of a conceptual model
- the identification of the critical exposure route (what is to be protected?)
- a definition of accepted risk / reference (e.g. that drinking water requirements are fulfilled at certain point of compliance)
- a description of the questions to be answered and a listing of input data needed for the calculation (e.g. influence of the water permeability of the landfill top layer on concentrations at POC)
- the selection of the appropriate (mathematical-) model. The complexity of the model must be applicable to the vulnerability of the site and in compliance with the quality of the input data. In many situations a simple model may perform as

well as a highly sophisticated model, depending on the quality of the input data and the uncertainty in the conceptual model. Transparency is easily lost when using too complex models. When using complex numerical models, benchmark (preferably analytical solutions) calculations should therefore be carried out to facilitate evaluation of the result produced by a complex model.

- a consideration of sensitivity of modelling results (influence of assumptions)
- a knowledge of the restrictions imposed by waste management legislation (especially in the case of hazardous waste)
- requirements of end-users (are results easily understandable... "weakness and strength" of the modelling work). Here it is necessary to stress that the models only show an anticipated release from waste under certain assumptions. The scenarios should only be used to compare different scenarios and should not be taken as absolute estimates. There is always a risk that the modelling results give a too favourable or too unfavourable estimate of release due to chosen input data and assumptions. It is important that the end-users understand what the results stand for and how to use the results in an appropriate way in decision making.
- competence of modeller with sufficient background, model knowledge, references etc.
- a list of issues specific to the site in question: how are the background concentrations in the surrounding environment considered in the modelling?

Table 1: Steps in modelling.

Phase:	Information needed:	Results of calculations:	Requirements for proper modelling
1. Estimation of release from the waste deposit	- Measurements of release from waste sample using percolation & batch tests - Long term behaviour of waste (see below "geochemical modelling") - Landfill characteristics - Estimation of the water flows (filtration, surface water) in the actual waste deposit (e.g. taking in account the water permeability of the top barrier) - Determination of time scale, water flows of interest	- calculation of L/S as function of time - combination of L/S and the results of percolation test to indicate concentrations in leachate leaving the landfill (taking in account change with time e.g. due to break down of top layer)	- reliability of laboratory leaching data - realistic water flow estimates
2. Estimation of the transport in the unsaturated zone	- Water balance from phase 1 - Sorption properties of soil beneath the landfill - Calculation of transport to groundwater level beneath the deposit	estimation of concentrations in leachate in contact with groundwater beneath the landfill at different time periods	- good knowledge of model requirements - selection of proper model tools based on available input data - proper documentation
3. Estimation of the transport to the surface water	- water balance from phase 1 - influence of surface water collection system, treatment efficiencies, - information of surface water recipients to be included	estimation of concentrations in surface water at selected POCs in surroundings of the landfill at different time periods	see point 2
4. Estimation of the transport with groundwater to point of concern (POC)	- characteristics of groundwater flow (site-specific) - information of surface water recipients to be included - modelling of dilution of leachates	estimation of concentrations in groundwater at selected POCs as a function of time	see point 2
5. Geochemical modelling Estimation of long term behaviour of deposited waste	- Measurements of total content and leaching data (pH static tests) - Determination of environmental conditions (redox,....)	- indications of minerals dictating the leaching behaviour - indications of influence of external conditions (carbonation, redox change) on leaching behaviour	- good knowledge of chemical reactions - experience of model applicability - information of species included in database - proper documentation

Recommendations for modelling approach

Today modelling is not extensively used in decision making due to the need for case interpretation of results and model set up. Especially the expertise of the modellers is crucial. There is therefore a need for guidelines including descriptive examples on how to understand and evaluate the results in order to increase a broader interest and use of modelling results in practice in waste management.

The project group concluded that the TAC approach used in estimating the impact of a landfill or a landfilled waste material on downstream groundwater (or surface water) quality is a suitable starting point in modelling. The TAC-approach may be illustrated in figure 1, which shows three models coupled in series.

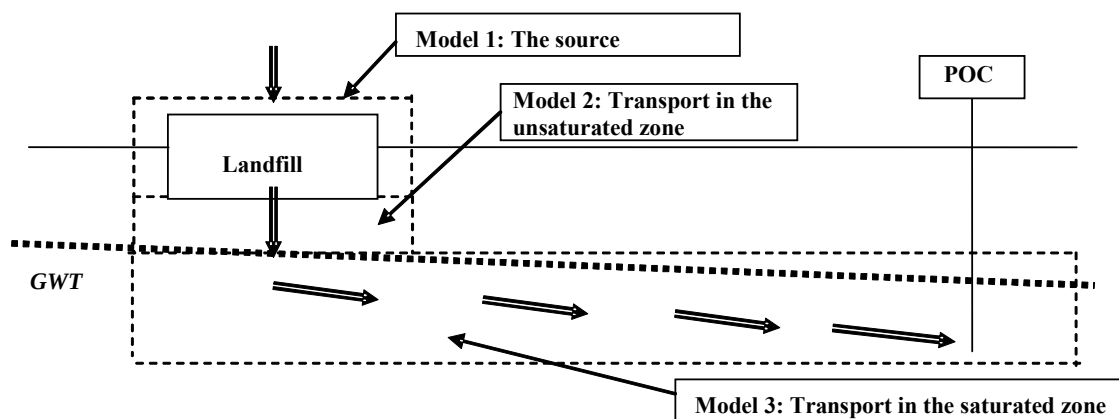


Figure 1: Cross-section showing the principle of using three coupled source and transport models for the calculation/estimation of the impact of a landfill on downstream groundwater quality (at the point of compliance, POC).

The TAC-methodology used to set EU criteria for landfilling may also be used for assessment of the impact of waste utilisation projects such as the use of alternative raw materials in roads and embankments. This would only require an adjustment of the source scenario to reflect the conditions of the site. In the development of EU methodology only the impact on groundwater was considered, but it may be just as similarly well useful in assessing the impact on surface water bodies (fresh water as well as marine waters). In this case a fourth model should be added to the series shown in Figure 1. The POC of the groundwater transport model is placed where the groundwater discharges into the surface water body, and the output from this model is used as input to a transport/dilution model for surface water body. A new POC needs to be defined in the surface water body and appropriate water quality criteria for freshwater bodies or marine waters can be used to evaluate the impact.

There appears to be a general consensus among regulators and users of impact assessment models that the methodology and conceptual models used in the setting of EU criteria for landfilling of waste was basically sound and generally applicable to assessment of the impacts of landfilling and utilisation projects on groundwater and surface water bodies. The actual models used may vary depending of the situation and degree of sophistication needed, and the input data and descriptive parameters may also be either general or site-and waste-specific. The concept is thus very flexible and it may be strongly recommended.

Modelling results are important tools for evaluations of environmental acceptance. However, in a risk evaluation related to the use of alternative materials in engineering earth constructions it might also be important to consider the total load of harmful compounds leached out to the environment. In some cases especially in utilisation scenarios, the modelling work should also cover other exposure routes, e.g. influence of dust emissions during construction and demolition of e.g. a road construction.

THERMODDEM A DATABASE DEVOTED TO WASTE MINERALS

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Abstract

With the growing trend towards reusing materials and with increasingly stringent environmental constraints, it has become essential that their behaviour should remain predictable throughout their life cycle. In this perspective, evaluation tests for prediction purposes are under development on a European level. However, a pertinent interpretation of data can only be accomplished through the use of purpose-built tools. Therefore, this preoccupation is currently being addressed by compiling a thermodynamic database specifically designed for waste. This can only be developed successfully provided contributions to it are obtained from a wide variety of sources and its use is coordinated amongst different laboratories, both in France and the rest of Europe. Its future objective could be to act as the cornerstone of a European expert system that allows the reactivity of materials to be modelled and their impact on the environment to be assessed in line with how they are used.

INTRODUCTION

In order to comply with European recommendations on the reduced use of mineral raw materials, it will be necessary, in addition to redesigning industrial processes, to recycle industrial by-products more efficiently. This reuse, however, will need to be ever more respectful of the environment, and the rules of usage will be increasingly restrictive. This is why, over the past several years, waste management policies have come under pressure to assess and forecast the physicochemical future of these substances. In concrete terms and at a European level, this has resulted in i) the establishment of standardisation approaches (acid-base neutralisation capacity measures, pH-controlled leaching, batch leaching, leaching by upward percolation, monolith leach tests) that are likely to provide the data needed to build models, and ii) a more generalised use of geochemical and hydrochemical numerical modelling.

However, the conclusions that can be drawn from these measures are quite mixed, due to the difficulty of achieving a coherent framework at a European level that makes possible the coordinated use of the different data derived from the proposed approaches: only the approaches necessary for data acquisition are standardised.

These conclusions show that much more effort needs to be devoted in Europe to this issue in order to i) develop shared expertise on leaching and related modelling on environmental impact, and ii) increase the level of knowledge so as to enhance the weight of French expertise within the different European think tanks.

APPROACHES

The empirical approach: potential and limitations

On the basis of experimental analysis (in batch or even in columns), the empirical approach consists in establishing empirical relationships that are able, in particular, to describe delaying factors. In this case, the evaluation of the potential pollutant is only valid for the conditions of the experiment. This type of approach poses a problem when it comes to extrapolating the experimental results to other scales, different scenarios, and longer timeframes. Its only advantage is its ease of implementation.

The mechanistic approach: potential and limitations

The mechanistic approach consists in forecasting the transformation of the “waste system” (source term of the pollutants) using geochemical models. It requires a precise analysis of the mineral phases present in the source (nature, quantity, possibly crystallinity) and knowledge of the solubility product of these phases. It also requires experimentation (batch and/or column) in order to design, then validate, the geochemical model. This approach has the considerable advantage of being independent of experimental conditions (the solubility products are the intrinsic parameters of the minerals) and of being adaptable to different space and time scales according to the planned scenarios. For a given scenario, sorption phenomena that can control the concentrations of certain pollutants can be taken into account.

The difficulty posed by the latter approach arises mainly from gaps in the classic databases concerning the solubility products of the phases under consideration, and this, for a number of reasons:

- Mineral waste consists of artificial products. Although the classic thermodynamic databases of geochemical models are well suited to natural minerals, they are less so when it comes to certain mineral phases contained in the waste. Amongst these, some are crystallographically close to the mineral phases in natural minerals, but differ from them in the elements they contain; others are very rare or even unknown in natural environments.
- The mineral phases in the different types of waste are commonly represented by solid solutions, something that implies a relative variability in their chemical composition within a given waste material.
- The same phase can be present in the same sample with various degrees of crystallinity, ranging from a crystalline form to a vitreous, or even a hydrated amorphous form.

To these crystallographic complexities is added the kinetic aspect. While it may be possible to disregard this in the scale of geological time, i.e. when dealing with hundreds of thousands of years, kinetics can become a key parameter in the short term that must be taken into account.

Currently, no database includes the specificity of mineral waste. This gap poses the major obstacle to developing the mechanistic approach, which provides information that is easier to extrapolate and more predictable than with the empirical approach and can provide, should that be necessary to the decision-making process, much higher-quality information.

THE PRINCIPLE BEHIND THERMODDEM

The measures taken as part of the THERMODDEM project with the intent to fill this gap centre around a fundamental task, the creation of a database of thermodynamic constants applied to mineral waste (Figure 1), and making this available on a website devoted to mineral waste.

However, to achieve this objective, several tasks are prerequisites:

- Compile a chemical-mineralogical database on mineral waste resulting from chemical and/or thermal processes and draws up a typology for this waste.
- On the basis of the typology and, through analysis of data from the literature, determine the main possible reaction paths.
- Compile from chemical and mineralogical literature all the solid-solution models available and applicable to the minerals present in waste.
- Extract essential facts from all existing models used to assess the thermodynamic data on mineral phases.

Once the prerequisites have been established, constituting the know-how capitalisation phase, it is then possible to populate the thermodynamic database applied to waste material, starting from the compilation of literature data and/or assessments either by calculation or on the basis of experimental measurements.

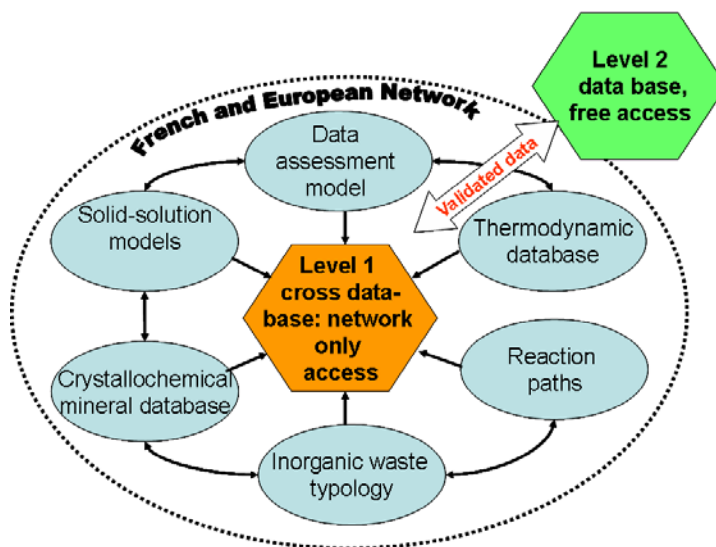


Figure 1 – Details of the content of the THERMODDEM database and its levels of operation.

Consistency and validation of the data is ensured by critical analysis of the values introduced into the database and by their use in modelling applied to the waste material.

Subsequently the kinetic aspect of the reactions should be taken into account by selecting the kinetic laws applicable to the different phases in waste or even by selecting the empirical laws appropriate to the context. Moreover, an assessment must be carried out to take into account the amorphous environment.

In its initial stage, the construction of the database proper is limited to inorganic compounds. Subsequently, it will be expanded, thanks to the potential of the European network organised around the project, to include the main parameters useful for organic compound speciation.

THE DATABASE AND WEBSITE

The database

Concerning mineral phases, three types of data will be provided in this base, to be made accessible on the web. The first category consists of mineralogical information and has two objectives, namely to inform or guide the user (in the choice of mineral phases and the interpretation of the behaviour of the system) and to aid in a critical review of the thermodynamic data; the chemical formula; the mineralogical family, the members of the family and the possible the poles for solid solutions; the polymorphs; the crystalline structure; and a mineralogical classification system (Dana's system was chosen). The second includes information on the thermodynamic properties of the mineral phases, with the objective of: providing data to generate specific databases (for computer codes); supplying information to generate data (ideal solid solutions); and

identifying sources. Lastly, are also provided, data on the occurrence of the mineral in natural or artificial environments, providing the base's user with references on the phase's actual range of stability (Figure 1).

In addition to the base devoted to mineral phases, THERMODDEM also manages a base on aqueous species. This is crucial, not only to supply the data necessary for calculating reaction properties, but also to generate code-specific databases. It includes standard individual properties at 25°C and 1 bar, the HKF³ parameters (or other formalism), complexation equations in the aqueous phase, standard reaction properties, a polynomial allowing the calculation of the evolution of an equilibrium constant versus temperature ($\log K(T) = A + BT + C/T + D \ln T + E/T^2$) and a grid of $\log K$ (0, 25, 60, 100, 150, 200, 250, 300°C) so as to generate and export files in formats compatible with the geochemical computer codes most currently used (PHREEQC, MINTEQA2, EQ3/6,...).

This database, prepared under Excel®, is then exported under Access®. Next, it is transformed under Oracle®, which handles data management for consultation on the website.

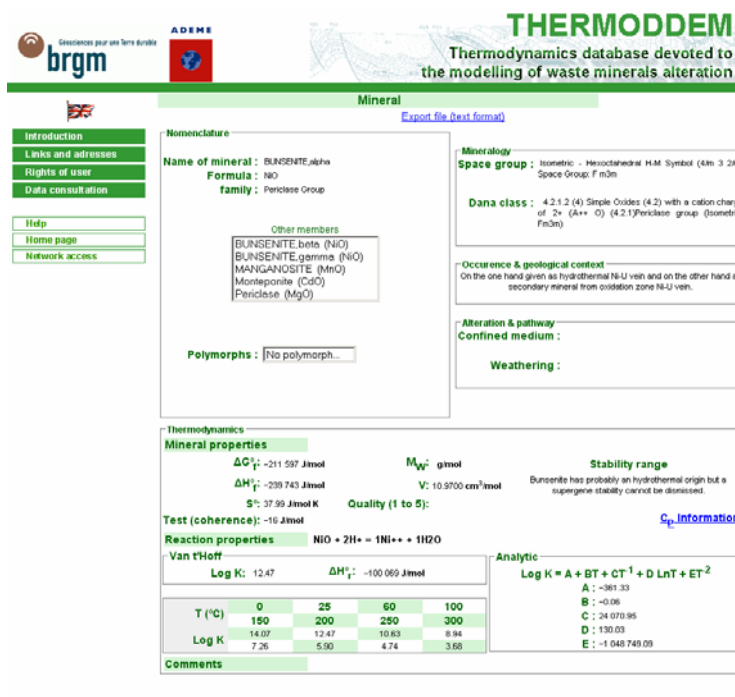


Figure 2 – Main window of THERMODDEM database.

³ Helgeson-Kirkham-Flowers, a formalism for the equation of state that describes the Gibbs free energy of the electrolyte as a function of increasing temperature and pressure.

The data management and harmonisation tool

With the Excel® format database, a management tool is associated that ensures mathematical coherency amongst the thermodynamic properties in addition to all the intermediate computations between these values and the reaction constants that are usable in the geochemical codes. Based on the use of macros programmed in Visual Basic, this management tool ensures:

- The automatic expression of the reaction in terms of the chemical formula of the complex or the mineral and of the basic species.
- The transposition of formation data to reaction data.
- The computation of reaction data according to the chosen primary species (with a possibility of creating a base of the desired aqueous species).
- The calculation of the phase transition properties for the minerals in question.
- The calculation of the properties of the aqueous complexes according to HKF formalism, which allows the thermodynamic properties to be calculated, and hence the stability of the aqueous complexes at high temperature (up to 300°C in the THERMODDEM framework).
- The calculation of coefficients A, B, C, D and E of the polynomial relationship that allows the equilibrium constant versus temperature to be obtained.
- The constitution of a text file usable as a database by the PHREEQC code or others.
- Tests of the various options.

In short, the tool makes it possible to go from the fundamental thermodynamic properties to the reaction constants in the aqueous phase, which to the best of our knowledge makes it a unique tool. It has also been designed to automatically update all the constants used by THERMODDEM, in case a correction is made in the fundamental properties of a basic species [i.e., Al^{3+} , Si^{4+}].

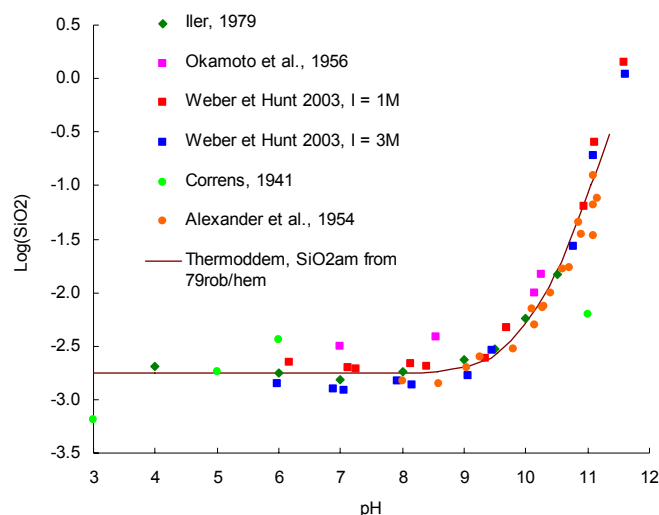


Figure 3 – Assessment of the silica speciation model and the amorphous silica solubility.

The core of the thermodynamic data in THERMODDEM is derived from the work of Helgeson et al. (1978), Shock et al. (1997) and Sverjensky et al. (1997). These are combined in the SUPCRT base, subsequently renamed Slop98, which was integrated into THERMODDEM. Furthermore, the base is periodically updated to take into account more recent work. So far, this effort has concerned the following elements:

- Si, Al, Mg, Ca, Na, K, C, S and Cl for the major elements,
- Pb, Cd, Co, Sr and Cr for the trace elements.

Future developments could involve the major elements Fe, P, N and F and a review of Ni, Cu, Cs, Zn, Hg, Ag. A special effort is made, for each phase that is introduced, to supply information on the properties that allow the influence of temperature to be taken into account.

The principle first entails the selection of the aqueous complexes and their most pertinent thermodynamic properties. Then the same is done for the solid phase, amorphous silica in the case presented above (Figure 3). Lastly the whole is tested on the basis of experimental work concerning the solubility of amorphous silica.

The special case of saline systems

Certain waste materials contain highly soluble phases. When these materials enter into contact with water, the salts are dissolved, which may generate strong ionic forces. In these cases, such classic activity models as Davies and Debye-Hückel are no longer valid, and more suitable approaches must be sought. Best known of these is the Pitzer approach (1973) that relies on the semi-empirical representation of the specific interactions amongst the dissolved species.

This approach, which differs from those followed for dilute solutions, requires its own database, at least to calculate the activity coefficients for the aqueous species. The equilibrium constants for both homogenous and heterogeneous reactions must remain coherent between the two approaches. The maintenance of a database adapted to saline systems is one of the tasks currently being carried out so as to ensure a wider scope of applications for the THERMODDEM tool.

CONCLUSIONS

The objective of a thermodynamic base devoted to waste, addressed in line with a deontology developed for THERMODDEM (data harmonisation, the identification of mineralogical families and groups, the description of known zones of stability, capitalising on the data for different activity models, etc.) is an essential process to improve the reliability of modelling and prediction. Because it compiles simultaneously thermodynamic data and knowledge that has been gained (natural and artificial systems), it brings a new dimension to the apprehension of the values used and of the mineral combinations taken into account in numerical models. This base, initially comprising inorganic species, will subsequently be expanded to take into account

organic ones. But its successful development is contingent upon contributions obtained from a wide variety of sources and its coordination amongst different laboratories at a national and European level. Its future objective could be to serve as the cornerstone of a European expert system to allow the reactivity of materials to be modelled and their impact on the environment to be assessed according to how they are used.

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Coupled modelling of leaching tests and environmental processes applied to stabilized waste

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Abstract

The coupling between chemical and hydrodynamic release processes, as well as waste/environment long-term interactions, are explicitly considered in reactive transport modelling; which represents an interesting alternative to the traditional contaminant transport approach. The extrapolation of leaching test modelling to a disposal scenario of stabilized waste is investigated in the present study as a typical example. The reactive transport code HYTEC is first applied to dynamic leaching tests considering, simultaneously, the chemical evolution of pore water, the progression of mineralogical alteration fronts, and the concomitant release of elements from the waste. Distinct fronts of mineralogical transformations take place in a thin layer beyond the monolith surface. Consequently, element releases was sensitive to the node size of the simulation grid and improved by taken into account the feedback of mineralogical evolution on porosity and diffusion coefficient. In the second part of the study, this source-term model is integrated to a simplified waste disposal scenario using the same reactive transport code and assuming a defective cover and rain water infiltration. The coupled evolution of the waste chemistry and the pollutant plume migration are modelled assessing the importance of the cracking state of the monolithic waste using either explicit fractures or dual porosity.

INTRODUCTION

The assessment of inorganic wastes impact on the environment and their best management require the evaluation of their short and long-term behaviours in disposal and recycling scenarios. The coupling between chemical and hydrodynamic release processes, as well as waste/environment long-term interactions (water infiltration, alkaline perturbation, etc.) are explicitly considered in reactive transport modelling [1,2]. This represents an interesting alternative to the traditional contaminant transport approach which mainly uses pre-calibrated flux as source terms. Beyond the quantification of source terms, such a coupled modelling is of primary importance for the understanding of long term release mechanisms and the extrapolation of laboratory results to site conditions characterised by lower solution/solid ratios, site specific geometry, cyclic infiltration, ... [3,4] .

A solidified/stabilized (S/S) waste containing lead is chosen to illustrate the methodology, progressing from leaching tests and physical characterization of the waste to source-term and disposal simulations. All the calculations were done with the reactive transport code HYTEC [5]. This numerical code couples advective and diffusive transport of solutes, in (un)saturated porous media, to chemical reactions at equilibrium or with kinetic control. HYTEC is strongly coupled, e.g. the effective

diffusion coefficients and hydraulic conductivity change when mineral precipitation or dissolution modifies the local porosity. Thus, HYTEC allows accounting for clogging by carbonation, or to the contrary, for porosity increase by leaching of calcium hydroxide in the case of S/S monolithic waste.

MODELLING OF THE LONG TERM LEACHING TESTS

The porous reference material was obtained by solidification (1% PbO by weight) with a proportion of 3/4 siliceous sand and 1/4 Portland cement CEM-I. ANC and MMF batch leaching tests were carried out on finely crushed materials. The monolithic waste samples (4cm by side) were submitted within a reactor to a permanent renewal flow of 250 ml/h, with a pure water solution, in closed system conditions. Mineralogical and microstructural studies, performed before and after the tests, relied upon bulk chemical analysis, X-ray diffraction, and scanning electron microscopy (SEM).

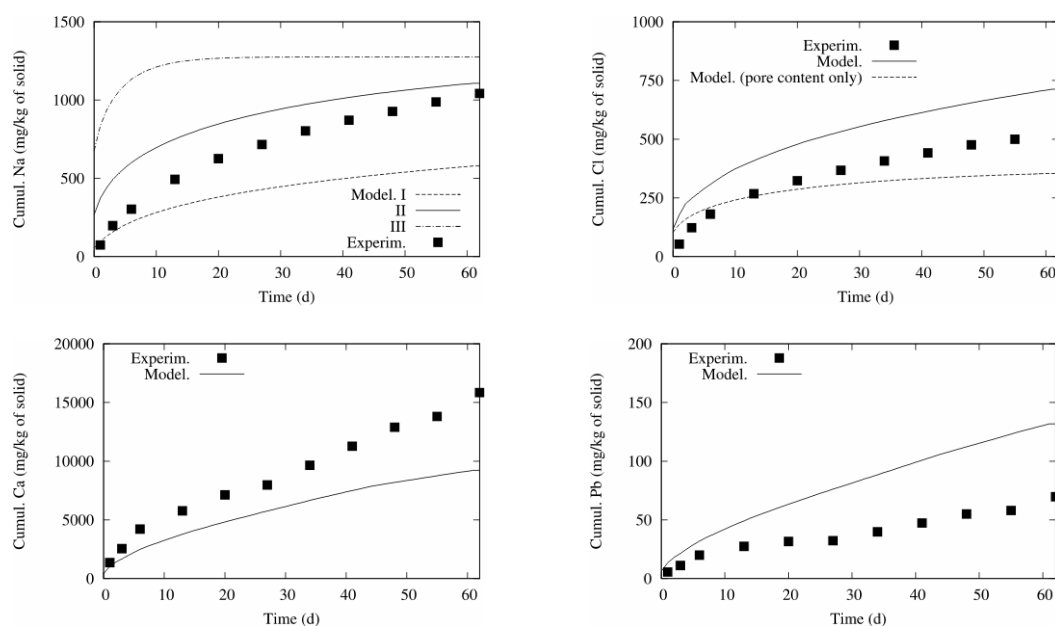


Figure. 1. Released cumulative mass of Na, Cl, Ca and Pb; the first graph is sensitivity analysis with respect to the effective diffusion coefficient ($De = 3 \times 10^{-10}$ (I), 3×10^{-12} (II), $3 \times 10^{-13} \text{ m}^2/\text{s}$ (III), see [8]).

Determining as accurately as possible the initial state (mineralogy and pore water chemistry) of the waste is a prerequisite for applying the model to different experimental or site conditions. The pore water chemistry of S/S waste was indirectly determined from the MMF test and mineralogy. A local equilibrium approach was considered in a first approximation due to high reactive surfaces of the crushed material. Sodium ions were assumed to be both dissolved in pore fluids and sorbed on CSH surfaces, whereas potassium ions were only introduced in pore fluids. Portlandite controls the calcium concentration in pore water. Dissolved silica is only controlled by CSH 1.7 whereas sulfate and aluminium are in equilibrium with ettringite. Chloride

was supposed to be present in pore water as well as in a Friedel's salt. The pH was calculated such as to maintain the electroneutrality of the solution. The bulk of lead was incorporated in the matrix of the CSH phases either by substitution or sorption [6], but its solubility was assumed to be controlled by secondary hydroxide phases. The extrapolation of these results leads to a pore water chemistry in the S/S waste enriched in Na-K as major cations and Cl-OH as major anions (pH ~ 13) ; lead concentration is about 60 mg/l.

The modelling of the closed-system DLMT set-up was made in 3D cylindrical geometry. Zero-flux boundary-conditions were defined at the lateral sides of the reactor, i.e. not at the S/S waste limits. The model considers, simultaneously, the chemical evolution of pore water, the mineralogical alteration fronts induced by the sequential dissolution of the cement hydration products, and the concomitant release of elements from the S/S waste. In good agreement with experiment, element releases (Fig. 1) were found to be mainly controlled by either diffusion (Na, K, and, to a lesser extent, Cl), by surface dissolution (Ca, Si) or by a mixed evolution (Pb, SO₄). All the calculated mineralogical transformations take place in a thin layer beyond the monolith surface. In agreement with experimental and modelling results [7], the deepest front corresponds to portlandite dissolution and CSH 1.7 transformation into CSH of lower Ca/Si ratio. A second, distinct and intermediate, front is made by ettringite dissolution. The network of CSH is globally preserved in the leached layer, complete dissolution occurring over a very small thickness only. Finally, hydrotalcite precipitation in the leached layer is expected by modelling due to pH drop.

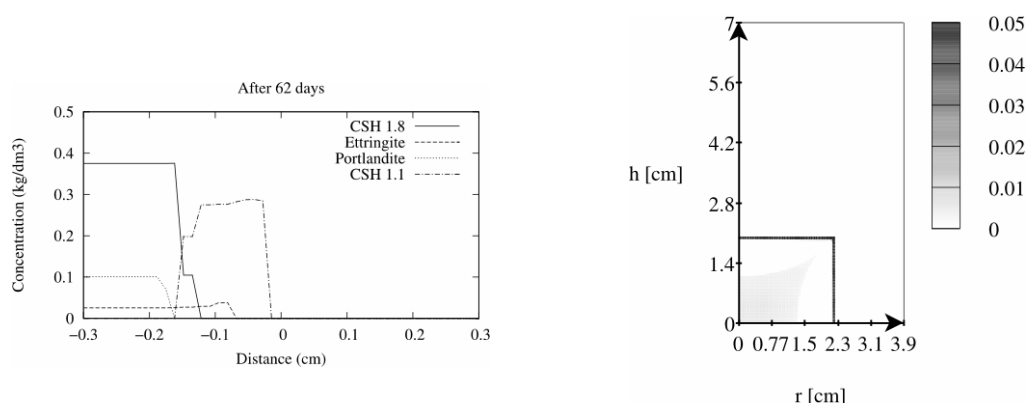


Figure. 2. Surface alteration of the monolithic S/S waste (1D profile, left) and precipitation of hydrotalcite (right) after 62 days (see [8]).

The monolith surface represents a singular zone of direct contact with the leaching solution are subjected to active dissolution/precipitation mechanisms. The reactive transport model can account for such processes, but CSH dissolution is prevented as long as portlandite is present in a node of the grid. Accordingly, the modelling of Ca, Si and SO₄ releases was quite sensitive to the node size of the simulation grid, contrarily to Na and K which are diffusion-driven (see [8] for further details). The modelling was also - qualitatively and quantitatively - improved by taking into account the increase of porosity and effective diffusion coefficient due to mineral dissolution in the leached layer [8].

LONG TERM DISPOSAL EVOLUTION AND POLLUTANT FATES

Hazardous waste repositories are complex engineering facilities. Our objective was only to illustrate how modelling may be used to extrapolate laboratory results to site conditions where environment factors yield waste evolution and subsequent pollutant release. In that respect, the disposal conditions was restricted to a subsystem zoom on the waste and the drainage system pessimistically assuming a defective cover – and therefore rain water infiltration. The simulations consisted in a 2D vertical profile including a micro-disposal (12 x 6 m) of metric-scale S/S monoliths with a leachate collector at its base. The grid node size was 0.1 m. Zero-flux conditions was defined at the boundaries of the collector. No boundary condition was assigned to the monolithic waste surface.

Extrapolation of source term derived from dynamic test to site conditions is far to be straightforward. The chemistry and the mineralogy of the waste monoliths were set exactly identical to those of the dynamic leaching tests and the reactive transport code HYTEC was used again. The coupled chemical evolution of S/S waste in the disposal and fate of the pollutant plume in the leachate collector are modelled assessing the importance of the cracking state of the monolithic waste yielded by ageing and temperature stress. The comparison of different cracking states is a relevant application of reactive transport model since cracks and fractures both increase rain water and carbon dioxide infiltration as well as L/S ratio and reactive surfaces of waste materials. A very low permeability was assigned to undamaged cement-based monoliths (test-case A), whereas fracture flow was taken into account using an explicit fracture representation considering a few main fracture crossing the disposal (test-case B) or a dual porosity approach for monoliths with a dense network of micro-cracks (test-case C). The physical containment of the disposal system decreases from test-cases A to C.

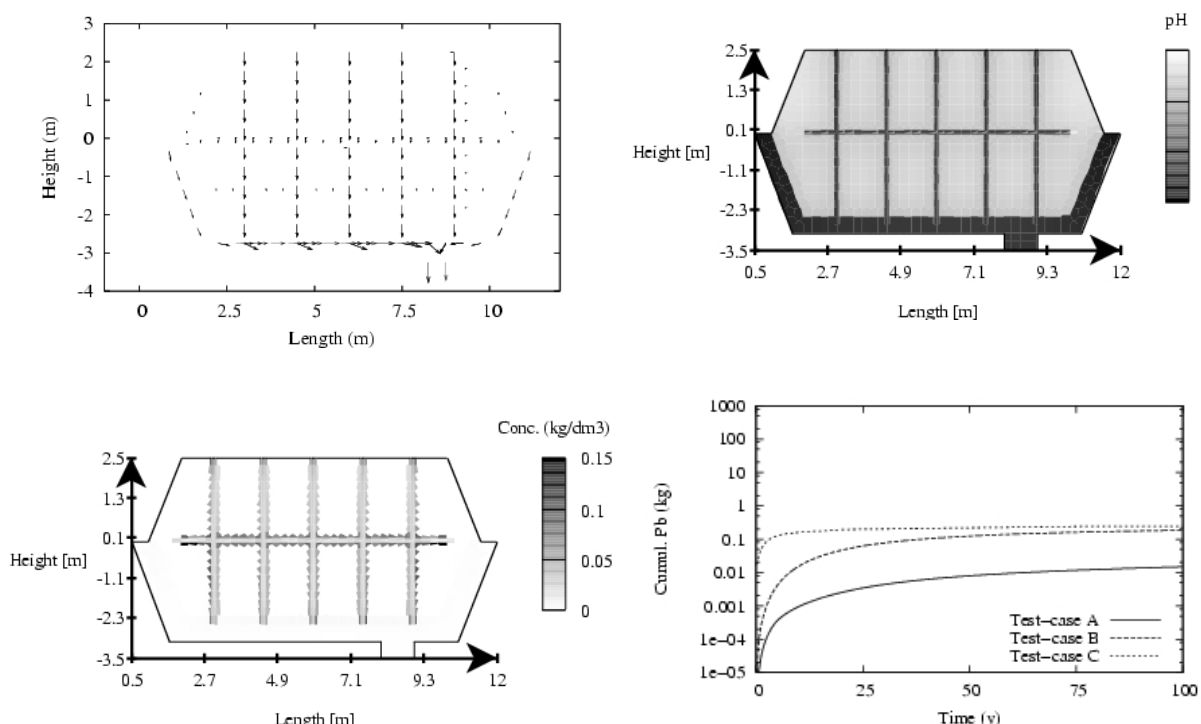


Figure 3. Darcy flow velocity (units in m/y), pH profile and carbonate precipitation in the waste/collector system for test-case B, as well as Pb cumulative release calculated at the collector base for all the test-cases (see [9]).

Fig. 3 exhibits the Darcy flow velocities calculated for test-case B. The occurrence of transversal fractures results in a channelized circulation within the waste zone and increase moderately the rate at the collector basement. The L/S increases locally in the fracture environment but remains globally low. The pH slowly decreases in the monolith matrix owing to the diffusion of alkaline ions in the main fractures and their subsequent advective transport to the collector bottom. The huge quantity of portlandite buffers on the long term the pH around 12.3, as in the MMF batch tests. However, pH is lower in the fracture environment due to water infiltration but, above all, CO₂ penetration. CO₂ reacts with portlandite yielding carbonation in the surrounding matrix, as shown in Fig. 3. The potential sealing effect at the fracture walls induced by carbonate precipitation was not considered. Fig. 3 also reports the calculated cumulative mass releases of Pb collected in the drainage system according to the three test-cases. Damaged monoliths can, at the extreme, release one hundred times more masses than undamaged S/S waste. However, even in test-case C, less than 0.1% of the total Pb waste inventory is released ultimately. Indeed, if the hydrodynamics of test-case C clearly favours lead mobility, at the same time this configuration leads to a quicker pH drop and therefore a sharper decrease of lead solubility in the matrix. Pb mobility in the overall system, fracture and matrix, is a combination of both aqueous chemistry and hydrodynamics.

CONCLUSIONS

Modelling the initial state of the S/S monolithic waste required a preliminary characterisation by mineralogical analyses and batch leaching tests. This core source term model was extended in a second step to simulate dynamic leaching tests considering, simultaneously, the chemical evolution of pore water, the mineralogical alteration fronts, and the concomitant release of elements from the S/S waste. In a third stage, coupling with environmental or field processes, such as rainwater infiltration within fractured monolithic waste, was achieved - to some levels of accuracy - with the same reactive transport code. The calculated contaminant and alkaline plumes can be seen as chemical- and time-dependent source terms for further simulations considering, for instance, clay liners and subsurface aquifers.

It is worth mentioning that this process-oriented modelling is still relatively complex and long to implement, requiring kinetic and thermodynamic data which are not always available. Nevertheless, this approach is clearly a powerful alternative to pre-calibrated source terms. It is furthermore enforced by the technical possibilities of reactive transport codes to deal with realistic geometries, boundary conditions and hydrodynamic regimes similar to those of (non reactive) contaminant transport codes. Additional studies are now in progress, to both simulate the open non saturated condition (sensitive to CO₂ diffusion, carbonation and clogging processes) or to extrapolate the methodology to MSWI bottom ash.

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Predicting Cr leaching from waste incineration ashes

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Abstract

As an example of an element which leaching behaviour has proved difficult to predict with respect to common batch leaching experiments. Highly varying solution concentration is typically observed. Cr leaching is proposed to be controlled by a number of coupled processes: release from the solid phase, reduction by metallic aluminium, and indirectly by the oxidation of metallic aluminium in the system. It is shown that sample pretreatment before batch testing can be used to tailor the resulting Cr concentration level in the test solution.

INTRODUCTION

Within recent years researchers and regulators have put increasing emphasis on developing laboratory tests to determine leaching from waste incineration residues as well as defining associated limit values to be used for regulating reutilization of the materials. The consequent focus on (geo)chemical aspects of leaching has over the years resulted in tremendous developments with respect to the understanding of the mechanisms controlling leaching from these residues. Now, it is generally agreed that the release of many elements is governed by precipitation/dissolution mechanisms, with influence from sorption in some cases. However, not all elements fit into this framework. One example is Cr.

Prediction or modelling of leaching from reutilized or landfilled residues is typically based on laboratory experiments, or in rare cases pilot scale experiments; the quality of the modelling results is greatly dependent on the ability to interpret test conditions and relate these to field scale conditions. The conditions in laboratory tests may or may not mimic real-life conditions; the trouble being that quantifying whether this is the case may prove difficult. Understanding the test conditions is in most cases the best option. This aspect is not always realized by authorities and researchers, potentially leading to false conclusions. Impact or risk assessments based on such test results are often done without accounting for the limitations inherent in the leaching tests that the assessments build upon, this may lead to limit values not reflecting the actual materials and utilization scenarios. Cr leaching is an element for which incinerators have had significant trouble meeting leaching criteria - even after ash treatment.

Several years of research on stabilization and leaching of waste incineration residues have shown highly varying leaching data for Cr (Chen et al., 2003). For air-pollution-control (APC) residues, no attempts have yet been successful in stabilizing Cr in the residues and thereby minimizing the leaching (Astrup, 2004). This makes Cr one of the most problematic elements in leachate from these residues and an element, which is generally not well understood with respect to leaching prediction.

The purpose of this paper is to discuss testing of Cr leaching from waste incineration residues, and the possibilities of predicting Cr leaching based on common leaching tests. The paper gives examples of Cr leaching data from APC residues and discusses these with respect to a new conceptual model on Cr leaching behaviour (Astrup et al., 2006).

METHODS AND MATERIALS

APC residues from a number of different Danish waste incinerators were investigated in batch experiments at liquid-to-solid (L/S) ratios of 5 and 100 l/kg. Residues were tested fresh as sampled and in some cases also after carbonation in order to reflect weathering effects. The Cr release from ash particles to the solution was monitored over 168 hours by sampling the aqueous solution at intervals, starting when residues and water was mixed. Traditional batch leaching tests were done at L/S 2 l/kg. Cr and pH was measured in the solution samples. Cr was measured in solution samples using Atomic Absorption Spectrometry.

RESULTS AND DISCUSSION

Cr chemistry

Cr in APC residues is generally considered to be present as Cr(VI) due to the oxidizing conditions in the furnace. Cr leaching from waste incineration residues has been observed to vary significantly and to be inconsistent (Cai et al., 2003; Astrup et al., 2006); typically in the range of a few µg/l to a few mg/l within pH 4-12 (Hjelmar, 1996; van der Sloot et al., 2001). It has been suggested that Al(0) may reduce Cr(VI) in ash systems (Abbas et al., 2001; Cai et al., 2003; Astrup et al., 2006), either because of Al(0) particles present in the ash or based on Al(0) actively added to the residues for stabilization purposes. Metallic aluminium has been identified in APC residues (Forestier and Libourel, 1998), and has been associated with H₂ generation in ashes (Lechner et al., 1997).

Al(0) may be oxidized by O₂ and water under alkaline conditions. In the case of anaerobic conditions, hydrogen gas is produced. Oxidation of Cr(III) by Mn-oxides is the main pathway for conversion of Cr(III) to Cr(VI) in natural systems. However, the alkaline conditions of APC residues cause Cr(III) and Mn-oxides to occur mainly as solids, thereby decreasing the Cr(III) oxidation rates. Astrup et al. (2006) argued that Cr(III) oxidation in APC residue systems was not important, but that the combined effect of Cr dissolution and reduction by Al(0) controlled the solution concentration. Additionally, Al(0) is affected by oxidation with O₂ and water.

Conceptual model

By investigating the release of Cr over time for 11 different APC residues, Astrup et al. (2006) found that the Cr release was kinetically controlled within a 168-hour experimental period and highly affected by the L/S ratio of the experiment, see examples of the release behaviour in Figure 1.

While most heavy metals are generally expected to reach stable concentrations within an equilibration period of 24 hours as is often used in regulatory batch leaching tests, Astrup et al. (2006) showed that Cr concentrations in some cases dropped significantly within the first 10 hours of water contact. This decrease was often followed by a much slower increase in concentrations towards the end of the experiment. Such a release pattern was observed in leaching tests at low L/S ratios with fresh residues. Thus, typical batch leaching tests on fresh residues at low L/S, such as L/S 2 l/kg, may likely provide relatively low Cr concentrations. Testing the same residues at high L/S ratios, Astrup et al. (2006) observed very different results as Cr concentrations now increased during the entire experiment. Carbonating the residue samples before leaching testing resulted in high concentrations throughout the experiments.

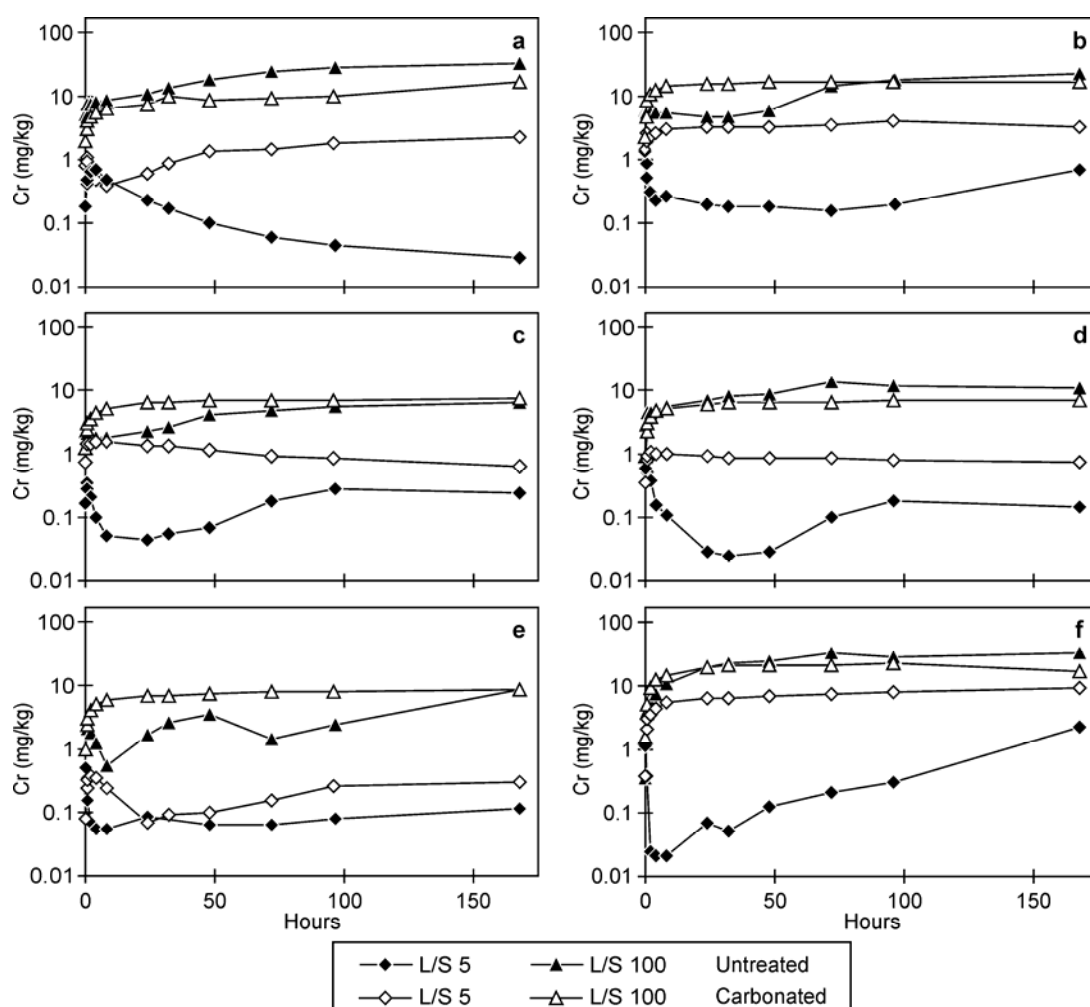


Figure 1. Examples of Cr release data. Cr concentrations were measured over time in batch tests with either untreated or carbonated versions of the APC residue samples a-f. Notice the large differences depending on the L/S ratio and sample treatment. After Astrup et al. (2006).

Astrup et al. (2006) proposed the following model to describe the observed Cr release behaviour in the investigated APC residues:

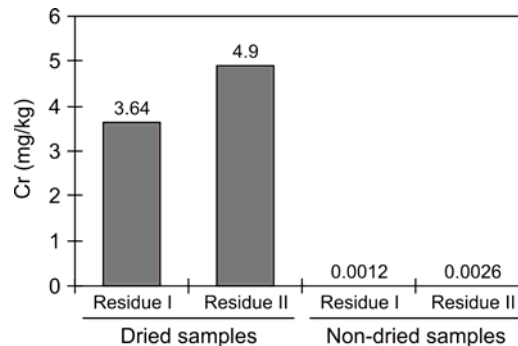


Figure 2. Leaching from two APC residues (I and II) were tested in L/S 2 l/kg batch tests with and without drying of the residue samples prior to leaching testing.

Erreur ! Des objets ne peuvent pas être créés à partir des codes de champs de mise en forme.

Erreur ! Des objets ne peuvent pas être créés à partir des codes de champs de mise en forme.

where $Al(0)_r$ denotes $Al(0)$ that is available for oxidation by $Cr(VI)$, O_2 , or water. The associated first order rate constant is k_{Al-ox} . $Cr(VI)_s$ is the solubility of $Cr(VI)$. The rate constant for $Cr(VI)$ dissolution is k_{Cr-s} , and the rate constant for $Cr(VI)$ reduction is k_{Cr-red} . The reduction of $Cr(VI)$ is proposed to be second order with respect to the $Cr(VI)$ concentration and the amount of reactive $Al(0)_r$.

Astrup et al. (2006) found that Cr leaching in the APC residues could be explained by varying the above rate constants, i.e. varying the relative importance of the involved reactions. Thus, Cr release at L/S 100 l/kg could be explained mainly by dissolution kinetics. The complex Cr release behaviour at L/S 5 l/kg for the non-carbonated samples was explained by a combination of $Cr(VI)$ dissolution and $Cr(VI)$ reduction. Although significant variations in release behaviour were observed among the residues investigated, the above model could explain Cr releases in all experiments, see Astrup et al. (2006).

Example of Cr leaching test data

With reference to the Cr release experiments performed by Astrup et al. (2006), Cr leaching was investigated in the L/S 2 l/kg batch leaching tests (EN 12457-1) used for regulatory purposes in Denmark, see Figure 2. Two stabilized APC residues were tested at L/S 2 l/kg according to the standard; however, in one case the samples were dried before testing while in another case the samples were not dried. In the latter case, the water content in the residues was accounted for in the leaching test.

As seen in Figure 2, Cr leaching from the non-dried samples were orders of magnitude lower than the leaching from the samples that were dried. This behaviour is consistent with the above-discussed conceptual model, as the drying is likely to oxidize Al(0) particles thereby decreasing the rate of Cr(VI) reduction by Al(0). In the case where samples are not dried, Al(0) particles are left reactive thereby reducing Cr(VI) in the leaching test.

CONCLUSIONS

The current knowledge of Cr leaching behaviour suggests that a more balanced way of interpreting leaching data is necessary. Al-O₂-Cr interactions appear to be responsible for variations in observed Cr leaching from batch tests. Depending of the sample handling, Cr leaching from the exact same sample may vary several orders of magnitude. This means that the actual Cr data obtained from typical batch leaching tests may not reflect actual behaviour in real-life systems, and that the Cr leaching data from these tests may not be used for assessment purposes. Authorities and researchers are encouraged to be cautious interpreting Cr leaching data from batch tests.

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Leaching of contaminants from MSWI bottom ash used as sub-base in road construction: Results from a pilot scale test site

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Abstract: A large scale demonstration site for utilisation of municipal solid waste incinerator (MSWI) bottom ash as sub-base in road construction was operated during a three year period. For two different bottom ashes, laboratory and field determinations of accumulated leached amounts as a function of L/S showed a reasonable agreement for several salts and trace elements. Due to carbonation in the field sites or the drains, pH of the leachates from the field sites was generally lower than that of the eluates obtained in the laboratory tests, causing differences in the leaching of some of the pH-sensitive trace elements. Oxidation effects on the leaching of Cr were also seen, particularly near the edges of the field sites. On-site ageing effects further gave rise to differences between laboratory and field leaching of DOC and Cu. A slope of 2.5 % of the surface of the pebble-covered compacted bottom ash sub-base, gave rise to a substantial lateral flow of precipitation (surface run-off to infiltration ratios of 7:1 and 2:1 over a distance of 8 m).

INTRODUCTION

Bottom ash (BA) from municipal solid waste incinerators (MSWIs) is produced in large quantities in many countries, and must either be utilised or deposited in landfills for non-hazardous waste. In general, the bottom ash must meet both functional and environmental criteria to be accepted for utilisation. Acceptance at certain classes or sub-categories of landfills may also require testing and compliance with environmental quality criteria [1]. The preferred management option for MSWI bottom ash in Denmark is utilisation provided it can be carried out in an environmentally acceptable manner. Experience shows that the functional properties of MSWI BA in general makes it well suited as a replacement for virgin raw materials in road construction, particularly when used as a sub-base material.

The utilisation of MSWI BA in Denmark is regulated by Statutory Order no. 655 of 27 June 2000 on utilisation of waste products and soil for back-filling and road construction purposes. The Statutory Order distinguishes between 3 different classes of materials according their contents of potential contaminants (trace elements and salts) and the leachability of these contaminants. The conditions for utilisation become more restrictive with increased content and leachability of contaminants. The limit values for leaching of MSWI BA to be utilised have been derived by the Danish EPA mainly from assessments of the potential risk of impacts on groundwater downstream of the application. The assessments are based on the results of modelling of contaminant transport in groundwater for specified utilisation scenarios using the results of leaching tests as a constant source of contamination. Only dilution effects, no

retention of contaminants, are considered in the groundwater transport model used. Groundwater quality criteria are to be met at a point of compliance 30 m downstream of the application, and a relatively low effectiveness of the cover (e.g. asphalt) is assumed [2].

The compliance or non-compliance of MSWI bottom ash with regulatory requirements for utilisation or landfilling thus depends on its behaviour in laboratory leaching tests. In predictive modelling of the environmental impact of utilisation or landfilling of waste materials such as MSWI BA laboratory column leaching data are often used directly or indirectly as the source term, assuming a substantial degree of similarity between the leaching behaviour in the laboratory and in the field. Since column leaching tests (e.g. the European test CEN/TS 14405) often are performed under conditions that may differ somewhat from field conditions, it is of interest to compare results of field observations with results obtained from laboratory column leaching tests. This paper will focus on the release of contaminants from two different MSWI bottom ashes under field conditions when used as a sub-base at the demonstration site and when tested in the laboratory prior to the application. Most of the information in this paper has previously been published [3]. Additional information may be found elsewhere [4, 5].

The work described in this paper was funded by DAFONET, a network comprising all MSW incinerators in Denmark.

THE FIELD SITES

MSWI bottom ashes from three different incinerators were built in as sub-base in six test sites ranging from 100 m² to 200 m² with top covers of asphalt, flagstones and pebbles, respectively. All sites except one were equipped with bottom liners and leachate collection equipment. The two sites discussed in this paper, site C (bottom ash from MSWI 1) and site E (bottom ash from MSWI 3), were covered with pebbles and equipped with LDPE liners, flow-proportional leachate collection systems and automated registration of the leachate flow. The main features of all the sites are summarised in table 1 and more details on the size, dimensions and amounts of MSWI bottom ash in sites C and E are given in table 2. The lay-out of units C and E are shown in figures 1 and 2. To enable the observation of possible edge effects, the liners under sites C and E have been divided into middle sections and edge sections, each with separate collection of leachate. The edge sections constitute the outermost 0.5 to 1.0 m of the bottom liners.

Table 1

Overview of the field demonstration sites and their main features. The two sites discussed in this paper (C and E) are shown in bold.

Site	Origin of BA	Major objective of site	Top	Bottom
A	MSWI 1	To study the rate of infiltration	Asphalt	LDPE liner
B	MSWI 1	To study the rate of infiltration	Flagstones	LDPE liner
C	MSWI 1	To study leachate quality as a function of L/S	Pebbles	LDPE liner
D	MWSI 2	To study leachate quality as a function of L/S	Pebbles	LDPE liner
E	MSWI 3	To study leachate quality as a function of L/S	Pebbles	LDPE liner
F	MSWI 1	To create and study a leachate plume	Pebbles	No liner

Table 2

Surface areas of sites C and E and information on the MSWI bottom sub-base layers.

Unit	Origin of BA	Surface area of site	Approx. thickness of MSWI BA layer	Dry bulk density of MSWI BA	Amount of BA in unit	MSWI
		m ²	m	tonnes/m ³	tonnes	m ³
C	MSWI 1	101	0.50	1.76	85.2	48.4
E	MWSI 2	98.6	0.54	1.85	93.0	50.3

The leachate runs by gravity from the bottom of the various liner sections through a water lock into pumping wells (see figure 3) from where it is pumped to a nearby storage and treatment plant for secondary raw materials where it is managed together with the surface run-off water. The amount of leachate pumped from each liner section is registered both by water meters and by the logging of pumping time. Sampling pumps, which are triggered by the level-controlled leachate pumps in the pumping wells, collect flow-proportional samples of the leachate from the different liner sections at each demonstration unit. The leachate samples are collected in 10 l polypropylene containers and analysed for pH and conductivity. Selected samples are analysed chemically for a larger range of constituents. Data on pumping time as well as water meter readings are stored in a computer and transferred electronically to the DHI at regular intervals. Climatic data are collected on site as well as from a nearby weather station.

UNIT B-E (division of leachate collection liner)

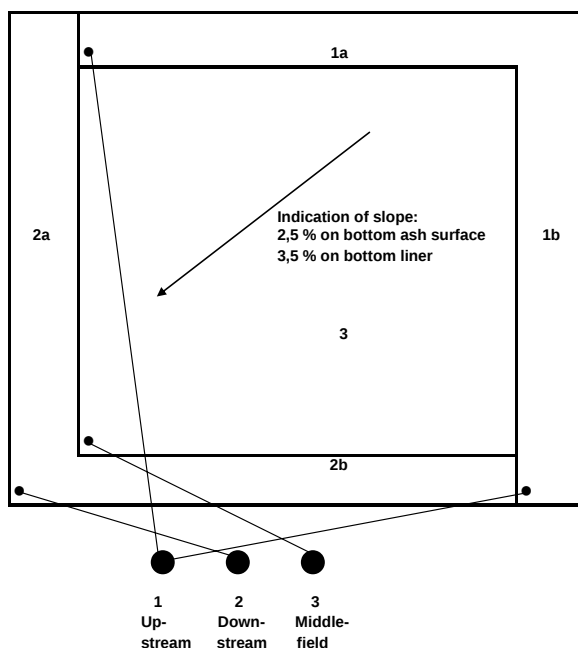


Figure 1
Layout of test sites C and E showing the bottom liner sections, the drainage systems and indicating surface slopes (from Hjelm et al. 2006).

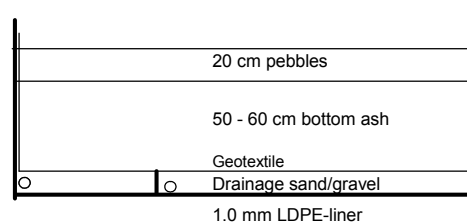


Figure 2
Cross section of the downstream end of sites C and E (from Hjelm et al. 2006).



Figure 3
Leachate collection and pumping well.

LABORATORY CHARACTERISATION OF THE MSWI BA

During the construction of the demonstration units, representative samples were collected of the MSWI bottom ash placed in each unit. In the laboratory, the samples were subjected to chemical analysis and leaching tests including column tests (CEN/TS 14405, single batch tests performed at L/S = 2 l/kg (EN 12457-1) and pH-static leaching tests (prCEN/TS 14997) performed at L/S = 10 l/kg. The eluates were subjected to a fairly broad chemical analytical program with special attention paid to constituents, which are particularly relevant to MSWI BA leachate (including sulphate, chloride, Na, K, Ca, Al, As, Cr, Cu, Mo (only in batch test), Ni, Pb, Zn and DOC (dissolved organic carbon)) as well as to components, which are regulated (further including Ba, Cd, Hg, Sb and Se). Only the results of pH-static leaching tests and column leaching tests are presented and discussed in this context. Additional results may be found e.g. in [3].

RESULTS AND DISCUSSION

Laboratory characterisation

In figures 4a and 4b the resulting concentrations of a number of components in the eluates from the pH-static leaching test are presented as a function of pH. Figure 5 shows the alkalinity of the two bottom ashes in the form of acid titration curves.

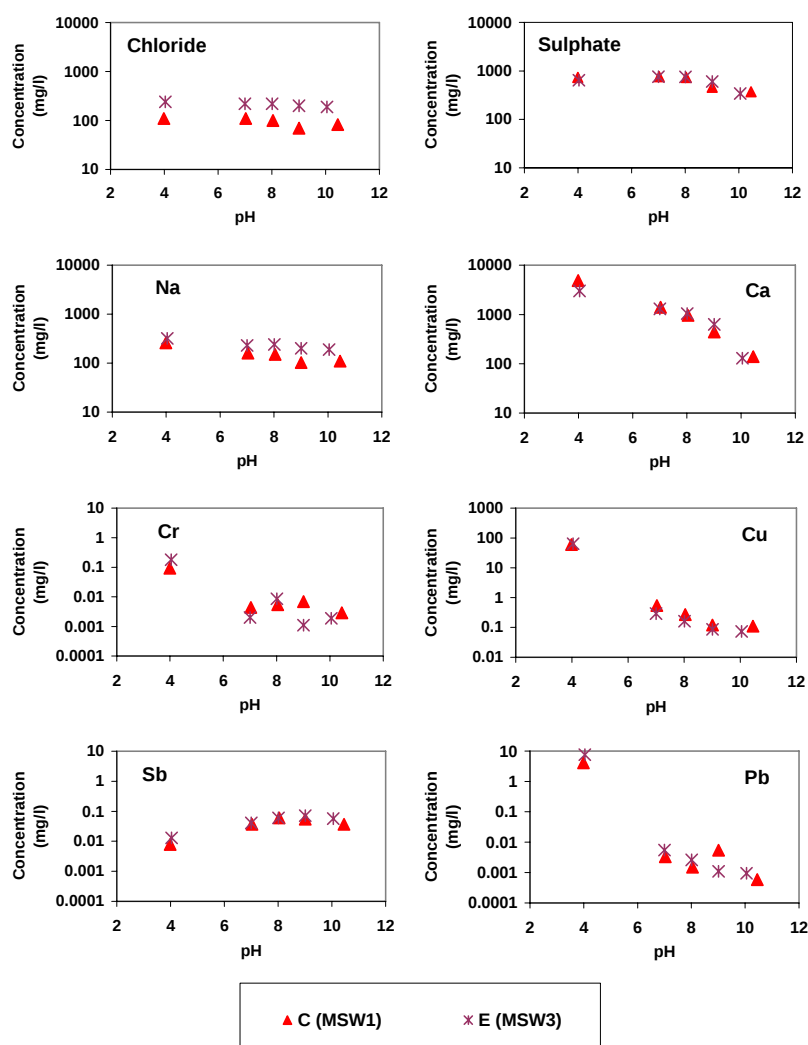


Figure 4a Results of pH-static leaching test (prCEN/TS 14997)

The results in figure 4a and 4b indicate that the result of a decrease of pH from the current values between 7.5 – 10.5 (see below) the concentration of most trace elements (but for instance not Sb) may be an increase in concentration in the leachate, unless it is reduced by other factors (e.g. adsorption and coating/diffusion). Acidification by carbonation may be expected to progress inwards from the surface of exposed parts of the ash, and figure 5 shows that the resistance against acidification is similar for the two ashes: 1.3 mole eqv/kg for C (MSW 1) and 1.2 mole eqv/kg for E (MSWI 3) for the entire mass.

The results of the laboratory column leaching tests (CEN/TS 14405) are presented in figures 6 and 7a and b together with the results of the chemical analysis of the leachates from the field sites.

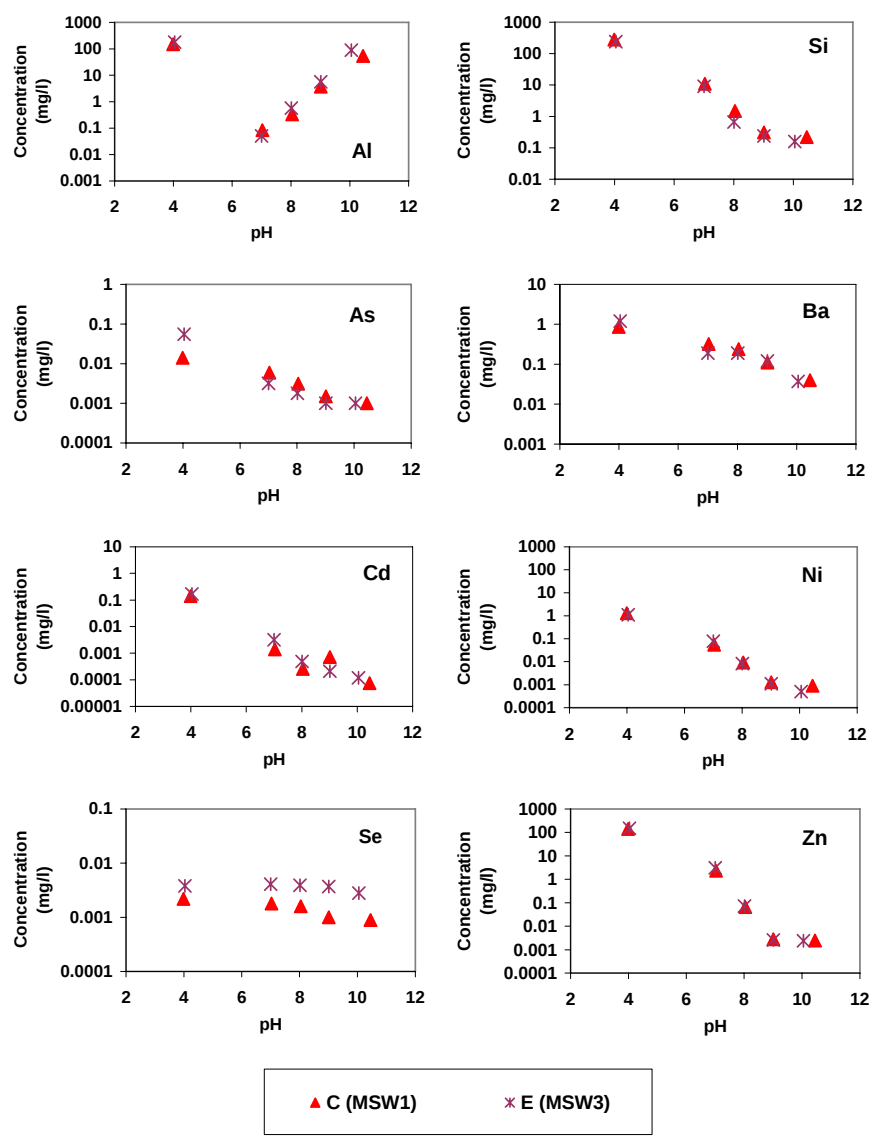


Figure 4b Results of pH-static leaching test (prCEN/TS 14997).

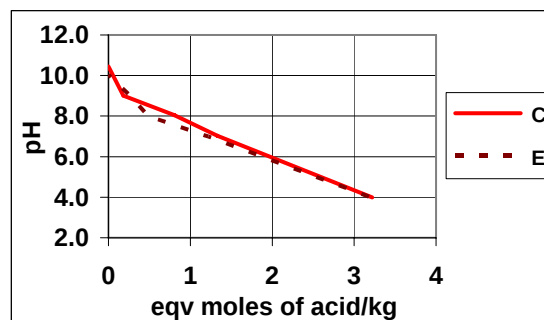


Figure 5 Alkalinity of bottom ashes C (MSWI 1) and E (MSWI 3).

Leachate composition: Comparison of field observations and laboratory results

Figure 6 shows pH as a function of the liquid to solid ratio (L/S) for the laboratory column tests on the bottom ashes C and E and for the leachate samples collected at the two field sites. Results are shown for the leachate from the upstream edges (C1 and E1), the downstream edges (C2 and E2) and the middle sections (C3 and E3), see figure 1. These leachates were collected automatically from the drain pipes over periods of weeks to months and accumulated in 10 l polypropylene vessels. Although exposure to air was restricted, carbonation of the moderately alkaline leachate could not be entirely prevented. To assess the potential effect of carbonation, samples were collected directly (over a few minutes) from the drain pipes during rainy periods in September 2004 and June 2005 as indicated in figure 6. The drain pipes are equipped with water locks to prevent intrusion of atmospheric air into the drain systems from the leachate collection wells.

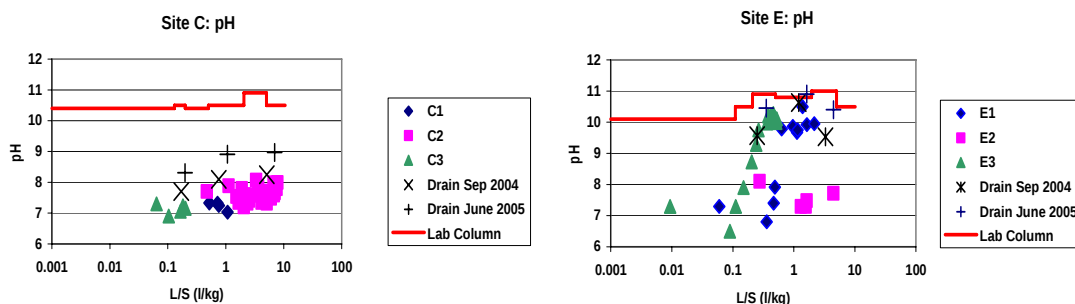


Figure 6: pH values measured in the leachates from the field sites and in the eluates from the laboratory column tests.

In figure 6 substantial differences of up to 3 pH units is seen between the column test results and the field observations.

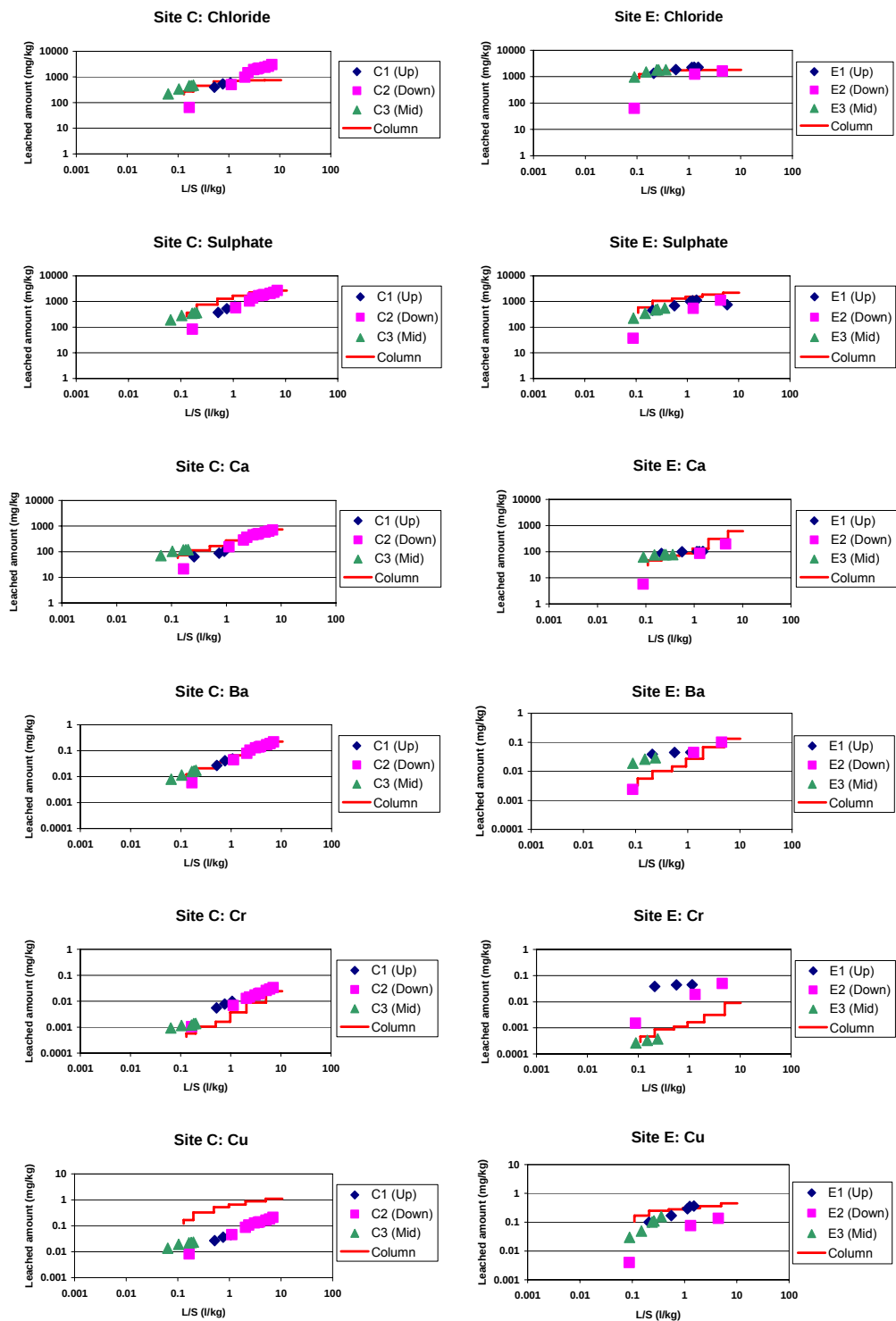


Figure 7a: Results of chemical analysis of leachates from sites C and E and column tests on the same bottom ashes performed in the laboratory. The results are shown as accumulated leached amounts as a function of L/S.

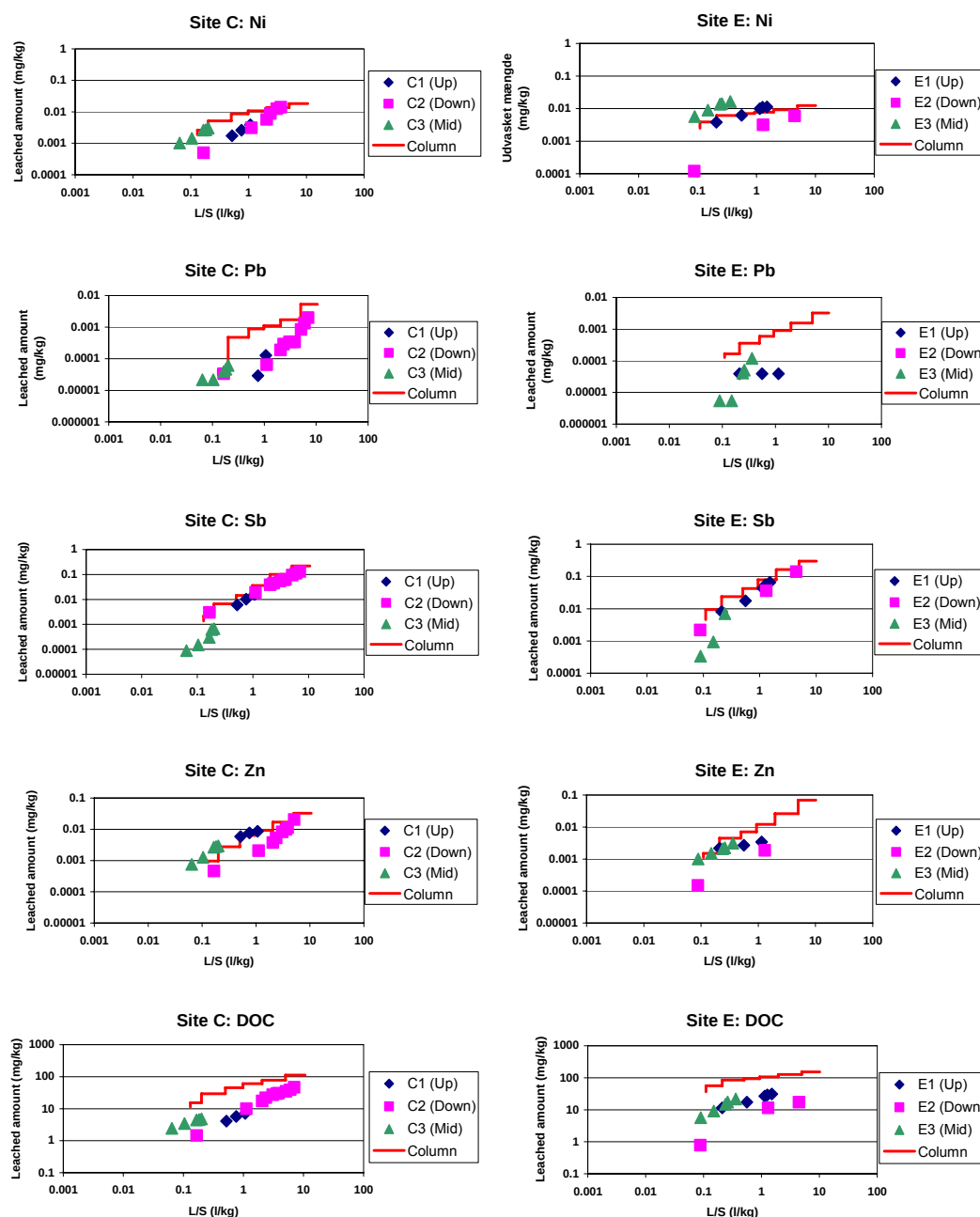


Figure 7b: Results of chemical analysis of leachates from sites C and E and column tests on the same bottom ashes performed in the laboratory. The results are shown as accumulated leached amounts as a function of L/S.

For bottom ash C, pH of the leachate collected automatically and the leachate collected directly from the drain pipes are the same or differ by less than one pH unit. This appears to indicate that for bottom ash C a substantial part of the reduction in pH happens within the site or the draining system itself rather than in the leachate

collection vessels during sampling. It should be noted that column tests performed on material dug out from site C in June 2005 led to pH levels in the eluate that were equal to or higher than those obtained in the original column test. The existence of preferential flow might explain this. However, the relatively good fit between (middle) field and lab results for some of the salts (e.g. chloride, see figure 7a) does not support the assumption of strong macro-scale channel formation, but possible the formation of channels in micro-scale.

For site E the initial difference in pH between field and laboratory results was similar to that for site C. However, during the progression of the leaching period, the pH values from the upstream edge section and the middle section approach the values obtained in the laboratory column test, and the pH values measured in the samples taken directly from the drain pipes are close to both field and laboratory values. The poor fit for the leachate from the downstream edges may be explained by edge effects and preferential flow.

For many of the contaminants for which data are presented in figures 7a and 7b, the fit between field results obtained over a period of 3 years and laboratory column leaching tests obtained over a period of one month is relatively good, particularly if only results from the middle sections of the field sites, which were designed to eliminate edge effects, are considered. Particularly poor fits are obtained for Pb for bottom ash E and for Cu and DOC for both ashes.

The results for Pb which is very sensitive to changes in pH (see figure 4a) may be explained by the observed differences in pH between lab and field results. DHI has carried out experiments that show that substantial reductions of DOC leaching (and decreases of pH in the leachate) may result from ageing of MSWI bottom ash. It is a well known fact that the leaching of Cu from MSWI bottom ash is facilitated by DOC, and the same ageing experiments also showed an associated reduction in Cu leaching. It is therefore likely that the discrepancies observed for DOC and Cu are caused by the reduction of DOC leaching induced by the ageing (biological and chemical changes) of the bottom ash. The correlation of Cu and DOC leaching is confirmed by figure 8 which shows the concentration of Cu as a function of the concentration of DOC for all column eluates and field leachates analysed for bottom ashes C and E.

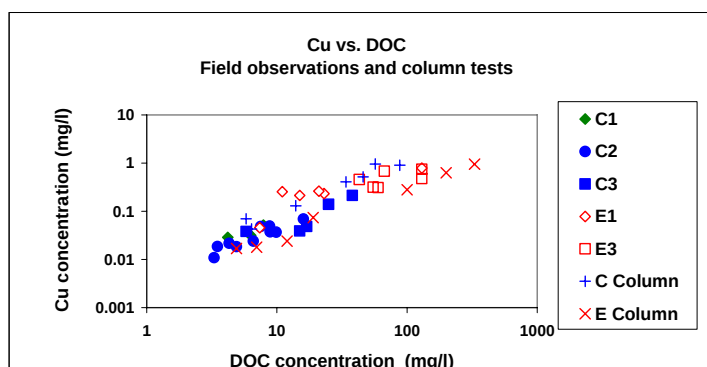


Figure 8: Cu leaching as a function of DOC leaching for all column test results and all field leachate observations for MSWI bottom ashes C and E.

For Cr a pronounced oxidation effect (C(III) oxidised to the more soluble C(VI)) is observed in the leachate collected from the upstream and downstream edges of site E, which are likely to be affected by channelling and preferential flow to a much larger extent than the middle section of site E, from where the leachate shows a much better fit with the column test, which was performed under conditions that did not accommodate oxidation.

Water balances

The water balances for test sites C and E the period September 2002 to October 2005 are shown in tables 3 and 4. The total precipitation during that period was approximately 2000 mm.

Table 3

Water balance for site C for the period September 2002 to October 2005.

Section of site	Percentage of surface	Percentage of leachate	Percentage of precipitation	Accumulated L/S ratio (l/kg)
C1 – upstream edges	24	15	11	1,2
C2 – downstream edges	20	78	57	7,8
C3 – middle section	56	6,8	5,0	0,20
C – all sections	100	100	73	1,8

Table 4

Water balance for site E for the period September 2002 to October 2005.

Section of site	Percentage of surface	Percentage of leachate	Percentage of precipitation	Accumulated L/S ratio (l/kg)
E1 – upstream edges	21	25	20	2.2
E2 – downstream edges	22	58	47	5.0
E3 – middle section	57	18	14	0,52
E – all sections	100	100	81	1.8

The water balances indicate that a substantial lateral flow of water occurs on or in the sloping surface of the bottom ash layer at both sites. The effect is most pronounced for site C where the middle section constitutes 56 percent of the surface area but only produces 6.8 percent of the leachate. Bottom ash E has a higher permeability than bottom ash C and at site C the middle section constitutes 57 percent of the surface area and produces 18 percent of the leachate. The water balances for the other sites were consistent with these findings [5].

CONCLUSIONS

Comparison of leachate monitoring results from two large scale field sites where bottom ash from two different MSW incinerators have been used as road construction sub-base covered by a layer of pebbles allowing infiltration of precipitation with the results of column leaching tests performed on samples of the bottom ash collected during the construction of the sites has shown some differences, particularly in pH, which generally is higher in the eluates from the column tests than in the leachates from the field sites. It is assumed that the differences in pH have been caused primarily by carbonation occurring within the sites and the associated draining systems, but despite efforts to avoid exposure to atmospheric air during the collection of samples, this may also have contributed to the reduction of pH in the leachate. For one of the sites, pH in the leachate has approached the column eluate values with time, whereas a substantial difference continues to occur for the other site. A reasonably good agreement between the leached amounts as a function of L/S observed at the field sites and in the laboratory column tests was found for several salts and trace elements, particularly for the inner parts of the sites which were less exposed to the atmosphere and less likely to exhibit strong channelling effects than the edges of the sites. Particularly poor agreements were found for Pb for one bottom ash due to pH effects and for DOC and Cu for both bottom ashes, probably due to the effects of ageing processes on DOC leaching in the field. A strong correlation between DOC leaching and Cu leaching was observed both for laboratory and field data. Differences in Cr leaching between the edges and the inner parts of one of the sites may be explained by oxidation. The results illustrate on the one hand that it is possible to get fairly good agreement between the results of laboratory column tests and field observations for many leached components. On the other hand, it also illustrates that it is important to minimise artefacts induced by experimental conditions, particularly exposure of material surfaces, alkaline leachates and eluates and leachates and eluates containing oxidisable components to atmospheric air. In field tests it is also important to be able to distinguish between the edges and the inner parts of a test body. Particular care should be taken with systems containing components that are sensitive to changes in pH and redox-potential.

The surface of the bottom ash had a 2.5 percent slope which gave rise to a substantial lateral flow on top of or in the upper part of the bottom ash layer. At one of the sites, the middle section constituted 56 percent of the surface area but only produced 6.8 percent of the leachate, and at the other site, the middle section constituted 57 percent of the surface area and produced 18 percent of the leachate. This corresponds to a surface run-off to infiltration ratio of 7:1 and 2:1, respectively, over a distance of approximately 8 m. The two ashes had different hydraulic conductivities, and at the first site, the amount of leachate produced constituted 5 percent of the precipitation during the period, whereas the amount of leachate produced at the other site constituted 14 percent of the precipitation.

Further work has been proposed to follow the leaching of contaminants, particularly from the middle parts of the sites, and to investigate the causes and effects of the lower pH in some of the leachates, and to follow the flow pattern. It is planned to compare the results to results of other field studies of MSWI BA, and to evaluate the data using LeachXS.

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Pilot scale data input in understanding and prediction of leaching behaviour of utilisation of waste in civil engineering

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Abstract

In order to assess the application of the ENV12920 standard [1], a study that lists and analyses main results of completed studies and R&D programs has been realized. The whole data set has been structured on a database form (ACCESS®) which allows doing requests on stakeholders, wastes, materials and/or utilizations and tests. This database is destined to future potential extensions.

Globally, this study has shown that the methodology often allows reaching a decision, concerning the utilization of a waste in a specific application for example, or the definition of limit values for specific applications ... Nevertheless, the critical analysis of each of the 10 studied programs put into evidence some fields of improvement to better perform this methodology:

- o description of the considered scenario and links with the choice of the studied influence factors are not often explained or described,
- o links between identified influence factors at previous steps and the performed tests are not always explicit,
- o the modeling step doesn't always end in a relevant or exploitable behavioral model towards data and influence factors,
- o validation tests are often performed, but their interpretation doesn't always allow to reach objectives, that is to say to validate the behavioral model.

One of the 10 studied programs is considered as exemplary with regards to the follow-up and the completion of the different steps. This program concerns the elaboration of fillers from stabilised MSWI fly ash used in different types of road applications with lab, pilot and full scales of experimentation [2].

INTRODUCTION

French context in the field of waste utilisation in civil engineering scenarios

As in all developed countries huge amounts of inorganic wastes are already used in France in civil engineering applications (coal fly ash, granulated or crystalized blast furnace slag,...). They are used in the framework of technical standards providing clear geotechnical requirements but almost nothing as far as environmental behaviour is concerned. Only two waste streams are covered by regulation (or regulation-like)

documents: foundry sands (July, 16 1991) and bottom ash from municipal waste incineration (May, 9 1994). In both cases only the release determined by the use of the X31-210 (French compliance test for landfill acceptance in force before the European standard EN12 457 is developed) is required.

With the increase of the landfilling costs following the hardening of the French regulation and the development of the notion of “final waste”, more and more wastes (mainly TPR: Thermal Process Residue) appeared as candidate to be used in civil engineering (glassy or crystallized vitrified waste, treated fly ash or even APC residue, non ferrous metallurgical slag,...).

It became absolutely necessary to develop and implement a comprehensive and rigorous environmental assessment approach for these new potential “construction secondary materials”.

Experts from University, School of Engineers, industrialists and environmental bodies (French Agency for Environment and Energy Management, ADEME) worked together in four main fields:

- academic research programs (pHD) on the mechanisms of stabilization and on the emission and transfer phenomenon from waste to environment. The positive role of Association RECORD (Waste Research Network involving industrialists and ADEME) is here to be mentioned (see the Nancy stabilization conference in 1995 and the SATB&ENV Lyon international conference in 1999)
- R&D programs around industrial needs for a given waste to be reused in different civil engineering applications in the framework of national or European programs
- development of “performance assessment procedures” dedicated to typology of materials (vitrified waste, solidified waste) by applied research bodies on behalf of ADEME
- capitalization and exchange on the results of both previous fields in the framework of standardization French commission (AFNOR). This leads to the development of X30-407 which was brought by French experts to WG6 when created and was the French contribution to ENV12920.

This short historical introduction explains that there was in France during the last 15 years a lot of efforts and a lot of people working together around this notion of “behaviour in scenarios”. Unfortunately this strong professional awareness has failed to be translated in regulation and 15 years after we have guidance documents recommending ENV12920 for monofills management or use of waste in road application (very recently and not yet in application), but no new regulations. This is one of the major reasons that supported the idea of making an analysis of the industrial applications during the last years on case-by-case basis and try to highlight the increase in knowledge gained thanks to ENV12920 or more generally thanks to behavioural approach and in addition the necessary methodological improvements to

propose in order to facilitate the use of this standard. This is the result of this work that is summarized in this document.

Critical Analysis

Considered items:

The critical analysis of the 19 combinations⁴ focused on the following 4 items:

- the quality of the scenario description: is the choice of the influence factors relevant? Has the influence of each factor been well assessed? (qualitatively and quantitatively)
- the application range and the utilisation limits of experimental tools: is the toolbox complete? Are essays complementary? Have they been performed according to standards or actual procedures (and mentioned in the report)? Is there a rational behind the global experimental approach (logic (chronological and/or methodological) between the different essays)?
- the application range and the utilisation limits of the proposed models: are the assumptions explicit, relevant? Has validation at pilot scale been realised? Is it conclusive and sufficient? Which uncertainties are attached to the predictions (scale effect)?
- the relation between the question (is it well defined?) and the conclusion of the program: does the program answer the question? Does it propose iterations with improvements of some steps?

Synthesis, determination of 3 fields of performing improvement

The critical analysis of each of the 19 studied combinations put into evidence three main difficulties linked to the performing of this methodology, that are detailed in the following paragraphs.

Scenarios description

The description of the considered scenario and the links with the choice of the studied influence factors are not often explained or described:

- there is often confusion between data relative to the scenario and data relative to the pilot. The scenario description is then often limited to the listing of conditions used in the pilot scale experiment (hydrous conditions, dimensions ...)

⁴ defined as: Waste / Role of the secondary raw material / Material / Scenario

- all the exposition conditions are not always identified and only the hydro geological and climatic conditions are explicitly generally mentioned. Information on mechanical, geotechnical, biological conditions are often lacking.
- the choice of influence factors considered in step 4 is often relevant towards the reality of the scenario, but the link between scenario description and listing of essays is not always explicit.

Those points put into evidence the necessity of redefining this step, by redefining the “scenario” term for example

Modelling step

The modelling of the leaching behaviour is a great research field of activity still in progress. The objective is here to consider the reality of the main mechanisms that occur during the leaching process in order to take into account the exposition conditions of the scenario. This results in mechanistic models more and more complex. The difficulty to express the influence of some factors (carbonation or other alteration for example) in terms of mathematical equations is higher.

In the same manner, the release of soluble species is often well modelled. For reactive species, the list of chemical equilibrium that play a role is often identified, but the complexity linked to the coupling of chemical and transport models is too important to allow a numerical resolution.

These facts are such that the modelling step doesn't always lead to a relevant or exploitable behavioural model with regard to data and influence factors.

Validation step

Pilot scale or full scale validation tests are often performed, but their interpretation doesn't always allow reaching objectives, that is to say validating the behavioural model.

Two reasons are suggested:

- in some cases, the proposed model is not comprehensive enough to propose a prediction in the conditions specified by the scenario. The pilot or field results are then simply compared to regulatory limit values in order to conclude on the environmental assessment.
- in other cases, validation test doesn't validate the proposed behavioural model: some unexplainable phenomena occur in the field test, and either the choice of influence factors or the validation test is not appropriate and it has to be done again.

The fact that real sites are not good tools to validate a model has also to be highlighted, because of the time scale of the real scenario in some cases, or because of the difficulty to instrument a real site, or because of unworkable results ...

Recommendations

According to these different points, recommendations can be made, like for instance:

- in the scenario description step, the distinction between the full documentation of the considered application on one hand and the description of a **conceptual model** that would constitute a simplification and a schematization of this application on the other hand,
- the identification and performing of **two validation levels**, the first one aiming at validation of the model at the conceptual model scale, and the second aiming at validation of the model at the considered application(full) scale

FILLERS ELABORATED FROM STABILISED MSWI FLY ASH USED IN DIFFERENT TYPES OF ROAD APPLICATIONS

Lab, pilot and full scales of experimentation

This program concerned treated fly ash from MSWI used as filler in different civil engineering materials. An innovative stabilization process (including washing/phosphatization and calcination) has been developed at the pilot scale by a big European chemical company involved in the production of reagents for the flue gas treatment and the road construction material have been designed and prepared by a major civil engineering international company.

POLDEN was in charge of the environmental assessment program at the lab scale and at the pilot scale.

This program is a full application of the European methodological standard ENV12920 [1], developed by CEN/TC 292, on the environmental assessment of pollutants emission of waste/material in disposal and/or utilisation scenarios. This paper focuses on the application of this methodology on treated fly ash used as filler in hydraulic-binder-treated base and the associated program is composed of 5 main steps:

- Step 1: Scenario and material descriptions
- Step 2: Determination of the effect of scenario's factors on release of material compounds by:
 - Intrinsic characterisation of the components availability (maximum available fraction)
 - Influence of chemical context on pollutants solubilization (prCEN/TS 14429)

- Study of the hydrodynamic of percolating systems (by the monitoring of a tracer)
- Study of the release dynamic at laboratory scale (prCEN/TS 14405)

- Step 3: Study of the behaviour in scenario by following a simulation test at pilot scale during 12 months

- Step 4: Modelling of the leaching behaviour in specified conditions and prediction of long term behaviour

- Step 5: Comparison of results obtained at different scales, data reconciliation.

This program has been performed on materials formulated by a civil engineering international company.

Scenario and material description

Scenario: Dimensions and implementation have been determined according to the technical specifications of a road base application and performed on the field test. At laboratory and pilot scales, the materials have been studied in a scenario without bearing course, that is to say in a scenario increasing the contact with water. 20 years has been chosen for the exposition time studied (estimated service life of a road).

Material: The fly ash-based material contains 12% of treated MSWI fly ash (by a specific stabilization process), 3,5% of a road hydraulic binder and 84,5% of natural limestone gravel. A reference material containing 4,5 % of binder has also been studied in order to compare release levels.

Both materials present values of permeability (10^{-5} m/s) such that the main mechanism to take into account when contact with water is percolation. This assumption is confirmed by pilot tests where no run-off water has been observed during the follow-up (even in simulated stormy periods).

Experimental program

Laboratory scale-study

Experimental program at laboratory scale can be divided in two parts:

- tests in static conditions (batch tests) aiming at determining intrinsic properties of materials,
- tests in dynamic conditions aiming at characterising elements release of constituents versus time.

Batch tests: Two batch tests have been performed:

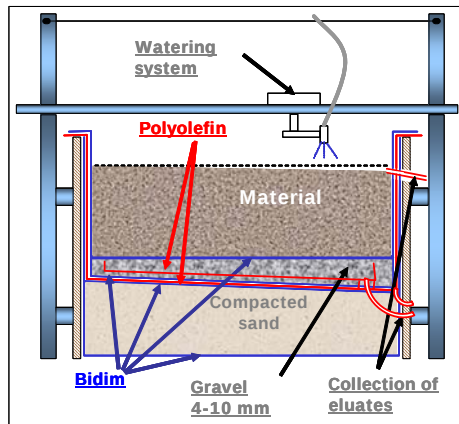
- the maximum available fraction test aiming at determining in three different pH contexts the quantities of pollutants that might be released. These values are used in the modelling step as maximum leachable quantities. The results provide also information on the intensity (efficiency) of the chemical stabilization.
- the influence of pH test (prCEN/TS 14429) aiming at determining the acid/base neutralisation capacity and studying the pH influence on pollutants solubilization. Otherwise, this test allows making assumptions on phases that control elements release.

Results show that chloride, sulphate and chromium are present in such quantities that release in conditions specified by the scenario must be studied. The study will focus on these species.

Dynamic test: considered materials seem to be monolithic porous matrices, but proved to be percolating systems. In order to characterise their release dynamics, they have been cooled in columns to realize up-flow percolation tests after setting time. The protocol was based on the prCEN/TS 14405 standard with some modifications (height of 20 cm as in scenario, filling and compaction of material adapted to these specific materials).

In order to determine the hydrodynamic parameters, a tracer has been introduced after the test and the restitution curve in outlet has been studied and modelled. Results of release, tracing and modelling are presented in the modelling paragraph.

Pilot scale-study



Two multi-parametric tests (road pilots) have been performed (on the treated fly ash-based material and on the reference material) in instrumented lysimeters of about 4 m² surface, subjected to controlled hydric regime during 12 months (see figure I). The chosen watering mode integrates different infiltration levels that correspond to different types of precipitation (continue fine drizzle, more important rain and dry periods).

The lysimeters are fitted out with an automatic watering system composed with a nozzle that moves on two axes in order to cover the whole pilot surface. Percolation and streaming eluates could be separately collected. The water balance, pH and conductivity were measured each week and eluates were analysed each month.

Figure I: Pilot scheme

Collected waters are only percolation eluates. After 12 months of following, about 45% of water has percolated and L/S ratio reached is 0,8 l/kg.

The pH observed are about 8 for the treated fly ash-based material (GHC) and 12 for the reference material (GT) due to the release of alkaline compounds from hydraulic binder and the buffering capacity of the treated fly ash.

As for laboratory tests, only chromium, chloride and sulphate are significantly released and could become problematic for the environment: modelling of their release is necessary.

Predictive modelling in scenario

Methodology

The fixed objective concerns the release prediction of major elements (Ca, SO₄²⁻, Cl⁻) and a trace element (Cr) in the conditions specified by the scenario. Modelling program can be divided in 3 parts:

- Determination of hydrodynamic parameters of percolating systems by using a tracer and modelling of the water flow,
- Determination of the phases controlling the release of considered species in the studied pH range,
- Coupling of chemistry and hydrodynamic by modelling the release.

Considered model

The transport of soluble species is governed by three phenomenons:

- Convection in the percolating porosity (open and connected pores),
- Dispersion due to structural and textural heterogeneity of the system,
- Exchanges due to the concentrations gradients between mobile zones (percolating porosity) and stagnant zones (semi-open pores or bad connected pores, or stagnant zones generated by an heterogenic flow in the percolating porosity)

The notion of stagnant zones can cover other mechanisms like dissolution kinetics, micro encapsulation or adsorption / desorption phenomenon.

The model used is the cascade of continuous tank stirred reactors (CTSR) with stagnant zones. It takes into account these three phenomenons and the coupling with chemistry [3].

Figure 2 presents experimental results of up-flow percolation, pilot and field tests and the corresponding simulations for the laboratory and pilot tests in the case of chlorides. The results are expressed in cumulated quantities in mg/kg as a function of cumulated L/S ratio in l/kg.

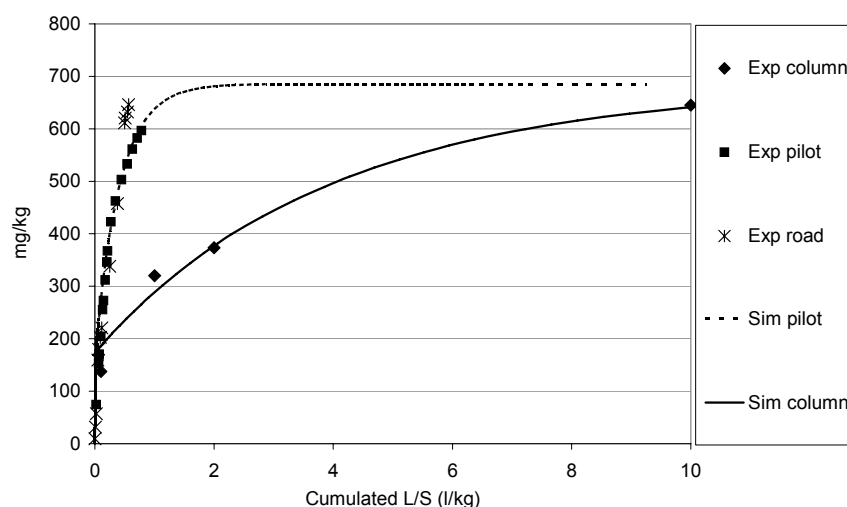


Figure 2: Extracted quantities of chlorides

CONCLUSION

The Environmental assessment program has been a full application of the European methodological standard ENV12920, developed by CENTC 292, on the environmental assessment of pollutants emission of waste/material in disposal and/or utilisation scenarios.

Main results of this study are:

- A good global retention of cationic heavy metals in the matrix has been observed and about 0,1% of chlorides and 1% of sulphates are mobilisable,
- At the laboratory scale, only chlorides, sulphates and chromium elements present releases such that a predictive modelling step is necessary,
- Modelling works have integrated different phenomenon that occur in the source term for soluble species: convection, dispersion and exchange between a percolating porosity and stagnant zones,
- The effect of hydric regime has been shown and quantified on the source term: pollutants mobilisation is globally more efficient (for the same L/S ratios) in real exposition conditions where wetting/drying occur in comparison with laboratory experiments (continuous water flow).

Acknowledgements

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Multiple-scale dynamic leaching of a municipal solid waste incinerator ash

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Abstract:

Predicting the impact on the subsurface and groundwater, of a pollutant source such as municipal solid waste (MSW) incineration ash, requires a knowledge of the so-called “source term”. The standardized laboratory upward-flow percolation test is generally considered as a relevant test for helping to define the source term for granular waste. The LIMULE project (Multiple-Scale Leaching) examined to what extent this test, performed in very specific conditions, could help predict the behaviour of waste at other scales and for other conditions of percolation. Three distinct scales of percolation were tested: a laboratory upward-flow percolation column (30 cm), lysimeter cells (1-2 m) and a large column instrumented at different depths (5 m). Comparison between concentration data collected from the different experiments suggests that for some non-reactive constituents (Cl, Na, K, ...), the liquid versus solid ratio (L/S) provides a means of extrapolating from one scale to another: if concentration data are plotted versus this ratio, the curves coincide reasonably well. On the other hand, for reactive elements such as chromium and aluminium which are linked by redox reactions, the L/S ratio does not provide a means of extrapolation, due in particular to kinetic control on reactions. Hence extrapolation with the help of coupled chemistry-transport modelling is proposed.

INTRODUCTION

This paper presents the main results of the LIMULE project (Guyonnet et al., 2005) that examined the influence of scale and percolation conditions on the mobilization of soluble constituents from a municipal solid waste (MSW) incineration ash. Three different scales of dynamic leaching were investigated. Upward flow laboratory column tests were performed according to standard CEN (2005). Two pilot-scale downward-flow percolation experiments were performed in lysimeter cells fed with demineralised water. A downward-flow percolation experiment was performed in a large column fed with demineralised water. This 5-metre high column and is made of 5 superposed cylinders equipped with ports for the monitoring of temperature, water content (TDR probes), capillary pressure (tensiometer probes) and fluid composition (porous cups). Concentrations in fluids collected from 5 porous cups (noted PC1 through PC5) located at different depths within the column, as well as at the column outlet, were monitored over time. Table 1 summarizes the main characteristics of the various experiments conducted under conditions of dynamic flow. A particular focus of the LIMULE project was the possible use of the L/S ratio as a means of extrapolating between scales and percolation conditions.

CHEMICAL COMPOSITION OF THE STUDIED WASTE

The waste studied within the LIMULE project is a furnace ash from a fluidized-bed MSW incineration plant. This ash was selected primarily due to its particle size which is close to that of sand. In order to limit the potential for material setting that might decrease the hydraulic conductivity and hence the ability to reach a significant value of L/S over the duration of the experiments, the ash was mixed in equal weight proportions with clean Loire river silica sand (0.1-1 mm), with a fraction < 80 µm lower than 1% in weight.

Table 1: Characteristics of the experiments performed under conditions of dynamic flow

Scale of experiment	Infiltration (cm/day)	Infiltration conditions	Duration	L/S reached
1: Upward-flow percolation column (30 cm)	15	Controlled	60 days	20
2: Indoor lysimeter cell (1 m)	0.55	Controlled	590 days	2.5
2: Outdoor lysimeter cell (2 m)	0.11 on average	Uncontrolled	610 days	0.3
3: Large column (5 m)	3.8	Controlled	580 days	3*

*: 3 at the outlet, but up to 24 in the uppermost porous cup

Major elements in the ash-sand mixture are related to the presence of Si-rich oxidized phases and to a lesser extent to the presence of Al, Ca, Fe and K (see Table 2). Trace elements in the ash-sand mixture are, by order of decreasing importance, Zn, Cu, Ba, Pb, Sn, Sr. The proportion of zero-valent (metal) aluminium is 1.4%. As will be seen below, this zero-valent aluminium has a major influence on the behaviour of chromium. From XRD analysis, the ash contains primarily quartz, silicates such as microcline, plagioclase, diopside, gehlenite, carbonates such as calcite, some sulphates (anhydrite) and iron oxides (hematite). Amorphous phases are also present and calcium phosphates were identified by microscopic analyses.

Table 2: Global chemical composition of the fresh sand, fresh ash-sand mixture and ash-sand mixture after leaching

%	LQ	Fresh sand	Fresh ash-sand	Leached ash-sand
Al ₂ O ₃	0.2	9.2	11.5	11
CaO	0.1	0.9	7.6	9
Fe ₂ O ₃ tot	0.05	1.58	3.64	3.2
K ₂ O	0.05	3.83	3.00	2.8
MgO	0.2	0.6	1.3	1.3
MnO	0.02	0.04	0.07	0.07
SiO ₂	0.2	80.8	67.4	60.1
TiO ₂	0.05	0.32	0.69	0.63
Al°	0.1	n.m.	1.4	0.54
Cl	0.01	n.m.	0.43	n.m.
C total	0.01	n.m.	0.2	n.m.
S total	0.01	n.m.	0.26	n.m.
mg/kg dry weight	limit	Fresh sand	Fresh ash-sand	Leached ash-sand
As	20	24	46	<
Ba	10	680	955	987
Cr _{total}	10	28	168	190
Cu	5	11	1021	1056
Ni	10	28	63	57
Pb	10	39	473	456
Zn	5	38	2053	2334

Notes: LQ = limit of quantification, n.m. = not measured, < = below limit of quantification,

RESULTS OF DYNAMIC LEACHING TESTS AS A FUNCTION OF L/S RATIO

In this section, concentration data collected from the various dynamic leaching tests are plotted as a function of L/S ratio and compared. Note that for a constant infiltration rate, the L/S ratio can be written:

$$L/S = \frac{I t}{d h} \quad (1)$$

where: I = constant infiltration rate, t = time, d = waste density, h = height of the waste column.

Figure 1 compares the evolution of pH, electrical conductivity and non-reactive (or poorly reactive) constituents (soluble constituents: Cl, Na, K, Ca) as a function of L/S ratio (based on collected outflow volumes). The pH is slightly higher in the large column

(11.5 - 12) than in the laboratory column (11) while the values from the indoor cell appear to fluctuate. Not shown in Figure. 1, the redox potential (Eh) increased gradually during the large column experiment from values around 0 mV at the start of leaching to values between 100 and 300 mV at the end of the experiment. The plots observed for soluble salt concentrations show a typical decreasing shape and a relatively good correspondence between experiments. The characteristic shape of the curves suggests that these constituents are rapidly dissolved and then gradually diluted by incoming demineralised water.

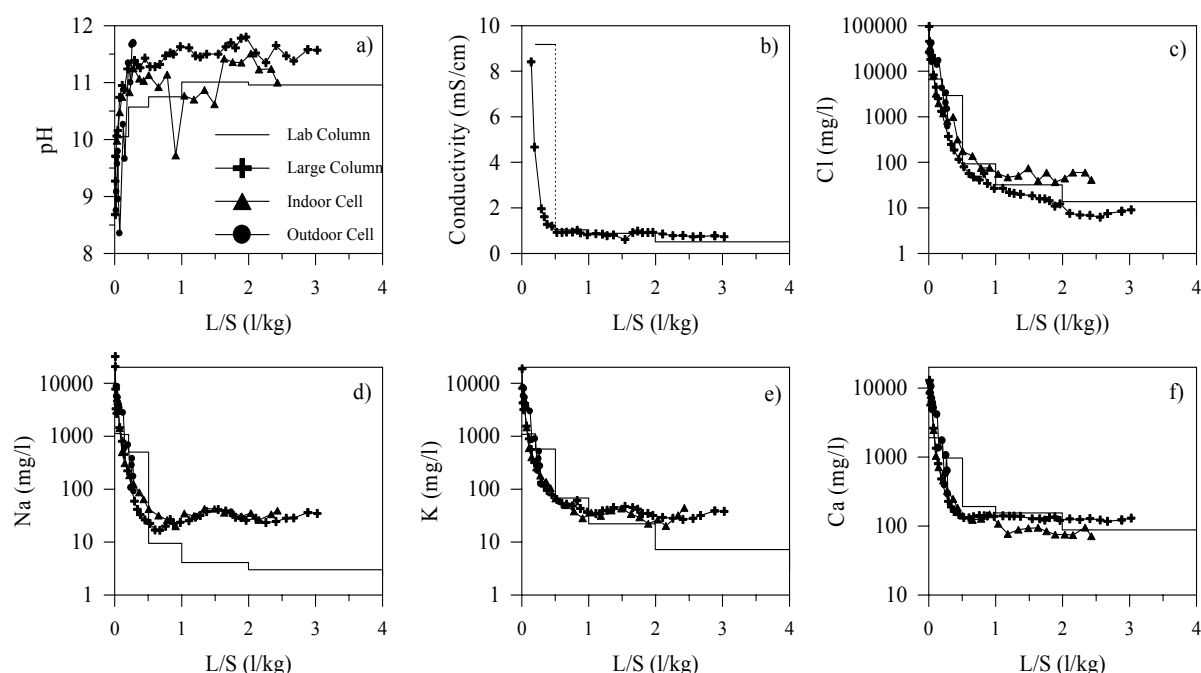


Figure 1: Comparison between results from dynamic flow experiments as a function of L/S ratio: pH, electrical conductivity and non-reactive constituents.

Figure 2 compares the evolutions of concentrations for reactive constituents. Unlike the non-reactive constituents, there is not a good correspondence between data from different experiments. Notice the inverse correlation between aluminium and chromium: chromium appears when aluminium decreases. This was observed in all the porous cups of the large column (see Guyonnet et al., 2005) and suggests the simultaneous oxidation of metal aluminium (Al^0) to Al(III) with a reduction of Cr(VI) to Cr(III) . So long as there is Al^0 to oxidize, chromium is in its less mobile trivalent form. These results are consistent with those of Chen et al. (2003) and Astrup et al. (2006) who performed batch tests on incineration residues and showed the oxidation of Al^0 in presence of Cr(VI) .

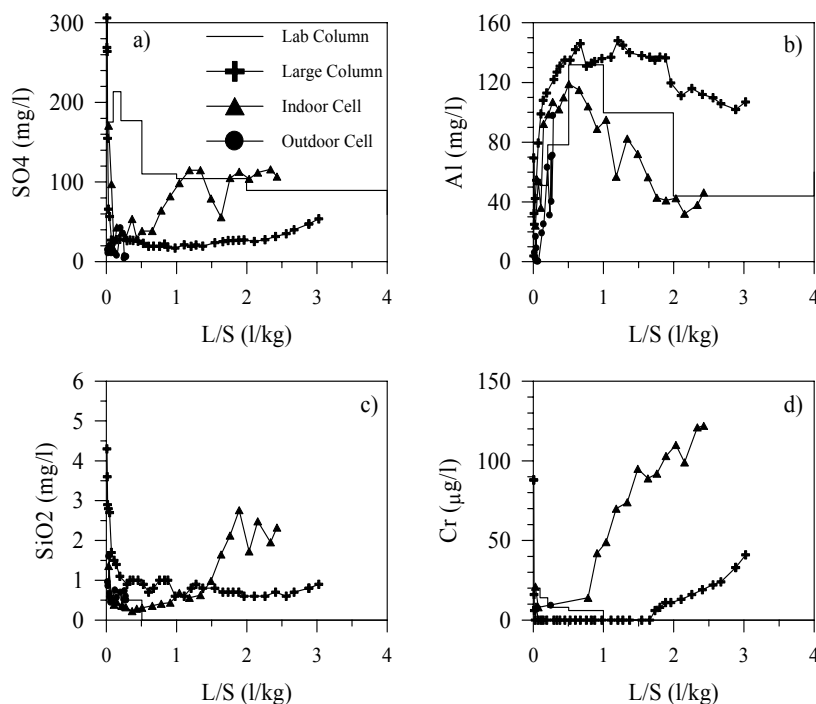


Figure 2. Comparison between results from dynamic flow experiments as a function of L/S ratio: reactive constituents.

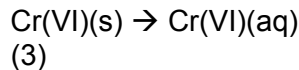
The relatively good correspondence between the data collected during the experiments performed at different scales and using different percolation rates suggests that the L/S ratio might be used as a tool to extrapolate between percolation scenarios. A good correspondence was also observed for certain trace elements: Ba and Sr (see Guyonnet et al., 2005). Data from experiments performed by Crest et al. (2005) on the same ash-sand mixture in column tests with alternating flow conditions also suggest a good correspondence for non-reactive constituents. On the other hand, for constituents that are influenced by reactions and reaction kinetics (see next section), the L/S ratio does not provide a means of extrapolation. This is observed here for aluminium and chromium, elements that are largely influenced by redox reactions, with specific reaction kinetics.

MODELLING RESULTS

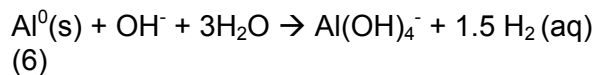
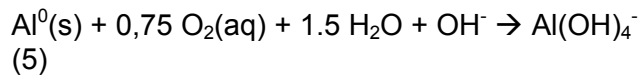
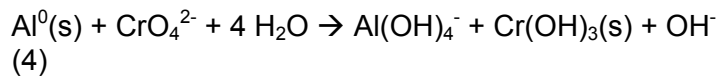
Since extrapolation between experiments using the L/S ratio is not satisfactory for the case of reactive constituents such as Cr and Al, a modelling approach was adopted. In order to attempt to reproduce the behaviour of these elements and provide a means of extrapolation, a coupled chemistry-transport model (PHREEQC; Parkhurst and Appelo, 1999) was used. The model couples dissolved constituent transport by advection and dispersion with chemical speciation reactions. The first step for performing such modelling is the identification of phases controlling solubilities and the selection of adequate thermodynamic data. Gibbsite ($\text{Al}(\text{OH})_3$) is generally considered to control the solubility of aluminium (Hsu, 1977, Eary, 1999). Comparison between geochemical simulations (Guyonnet et al., 2005) and aluminium solubility observed in the large

column suggest that the microcrystalline form of Gibbsite (Gibbsite(μc)) is a possible controlling phase. Next, several hypotheses were tested with respect to oxido-reduction of the Al-Cr couple, by confronting model results with the measured data. At the elevated values of pH observed (pH~11.25), it is hypothesized as in Astrup et al (2005), that chromium concentrations are the result of the following simultaneous and competitive reactions:

- kinetic dissolution of Cr(VI):



- Al^0 oxidation by Cr(VI), O_2 and/or H_2O :



where (s) and (aq) indicate solid and aqueous phases.

Oxygen and water were included as oxidants because, from mass balance considerations, experimental data suggest that another oxidant than Cr(VI) must be involved. The model takes explicitly into account the transport of aqueous oxygen (10 mg/l in the inflowing water) and the quantity of aqueous oxygen in solution is controlled by the oxidation of reactive Al, following:

$$\frac{d(\text{Al}_r^0)}{dt} = -k_{\text{Al-ox}} \left(\text{Al}_r^0 / M_0 \right)^p [\text{O}_2(\text{aq})]^q \quad (7)$$

with:

$$\frac{d(\text{Cr(VI)(aq)})}{dt} = k_{\text{Cr-s}} - k_{\text{Cr-red}} [\text{Cr(VI)(aq)}] \text{Al}_r^0 \quad (8)$$

where: Al_r^0 = amount of reactive metal aluminium at time t , M_0 = initial amount of reactive metal aluminium, $k_{\text{Al-ox}}$ = kinetic constant for the oxidation of metal aluminium, $k_{\text{Cr-s}}$ = rate of Cr(VI)(s) dissolution, $k_{\text{Cr-red}}$ = kinetic constant for Cr(VI)(aq) reduction, p = surface exponent and q = oxygen exponent (additional details regarding model parameters are provided in an article in preparation devoted to the coupled chemistry-transport modelling).

Stoichiometries of reactions (3) through (6) and kinetic rates were specified in the PHREEQC input file and the advective-dispersive equation was solved using a finite difference algorithm. Figure 3 shows the results of a match to data collected from the large column in porous cups located at two depths (PC3 at 254 cm and PC4 at 356 cm) and using the same values of fitting parameters: $M_0 = 300 \text{ mg/kg}$, initial available Cr(VI) in the solid = 1 mg/kg , $k_{\text{Al-ox}} = 2 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$, $k_{\text{Cr-S}} = 10^{-12} \text{ mol l}^{-1} \text{ s}^{-1}$, $k_{\text{Cr red}} = 4 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$, $p = 2/3$, $q = 1/2$. It is seen that the overall observed behaviour of aluminium decrease, coinciding with Cr(VI) increase, is reproduced.

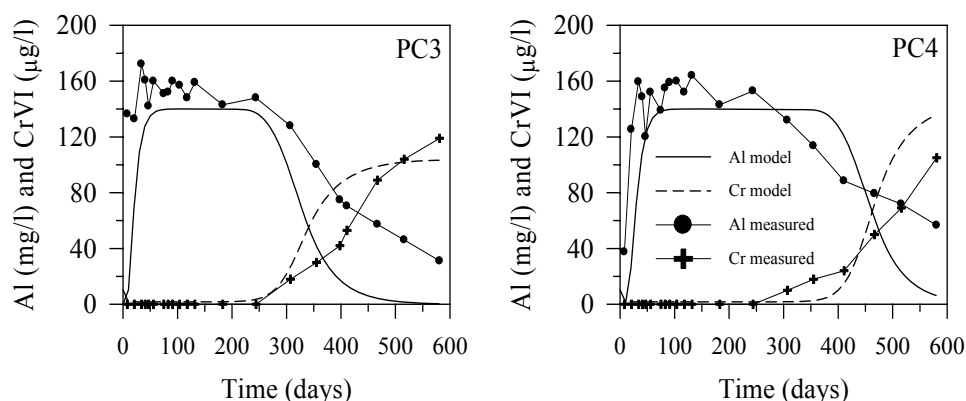


Figure 3. Comparison between measured and simulated concentrations of Al and Cr(VI) at two depths within the large column (PC3: 254 cm and PC4: 356 cm)

CONCLUSIONS

During the LIMULE project, it was found that the L/S ratio provided a means of extrapolation for the case of non-reactive constituents such as soluble salts (Cl, Na, K, Ca) but also for certain trace elements (Ba, Sr). When the concentration data are plotted versus L/S ratio, the curves coincide reasonably well suggesting that one curve can be used as a type-curve to provide a concentration versus time relationship for other percolation scenarios. For reactive constituents on the other hand, the L/S did not provide a means of extrapolation. This was found to be the case in particular for aluminium and chromium, two elements that are linked by redox reactions with specific reaction kinetics: oxidation of metal aluminium and reduction of Cr(VI) to Cr(III).

If the evolution of an element in solution is controlled by reaction kinetics rather than by the rate at which water is percolating through the waste, then using the L/S ratio to extrapolate from the small scale to the large scale will have the effect of overestimating times of element breakthrough (unconservative estimates; see Guyonnet et al., 2005). Considering that the L/S ratio does not provide a means of extrapolation in the case of reactive elements, it was proposed to extrapolate using modelling. Difficulty in simulating the behaviour of reactive constituents, such as aluminium and chromium, using a coupled chemistry-transport model, resides primarily in the number of parameters involved: stock of reactive metal aluminium that can be oxidized, availability of oxygen in the system, kinetics of the reactions of Al^0 oxidation and Cr(VI) reduction, choice of mineral phases controlling the solubility of aluminium and

chromium, selection of thermodynamic data for these phases, etc. While the modelling tool was found to be extremely valuable for exploring different hypotheses regarding mechanisms controlling the behaviour of Al and Cr in this system, truly predictive capability remains limited due to the complexity involved. However, the predictive capability of such modelling is increasing, provided it relies upon detailed characterization of the waste (see for example Kosson et al., 2002). For example, it was found in this project that reproducing the results of the pH-dependent solubility test (CEN, 2006) with a geochemical speciation model, could help considerably in guiding choices with respect to the selection of mineral phases to be included in the predictive modelling (Guyonnet et al., 2005). As the waste is solubilized during such a test over a large range of pH values, it yields a global response that provides information regarding the mineral assemblage controlling solubilities. By coupling this information with mineralogical observations, the model can be constrained and hence its predictive capability improved.

With respect to the source term, one essential piece of information for predictions of potential impacts is the maximum concentration value in the water emitted from the waste. The results from the various scales of experimentation suggest that, for a constituent such as chloride which has an enormous solubility and in spite of the equilibration period included in the standard test (CEN 2005), the first value of concentration measured in the laboratory test (at $L/S = 0.1$) does not provide an adequate estimate of the maximum concentration that can be expected during flow through a larger column of waste, where the first significant values of L/S may be much lower.

Considering the complexity of source term behaviour for the case of reactive constituents, the question remains as to the extrapolation of the standardized upward-flow laboratory column test to field conditions. Several options might be considered. Tests could be performed at different rates in laboratory columns of different sizes, thus providing direct information regarding extrapolation. Pilot-scale tests, that are more representative of true field conditions, can be performed, especially if laboratory results indicate that there is an environmental issue. In any case, characterization should be performed in parallel with the modelling effort since the ultimate objective is generally to be able to predict a potential environmental impact; such predictions necessarily rely at some stage on model calculations.

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- Parkhurst D.L., Appelo C.A.J. (1999) - User's guide to PHREEQC (version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculation. U.S. Geological Survey, Water-Resources Investigations. Report 99-4259, 312 pp.

Annexe 2

Transparents présentés (Presented slides)

RECENT DEVELOPMENTS IN CHARACTERISATION LEACHING TESTS AND GEOCHEMICAL MODELING TO DEFINE A SOURCE TERM FOR ASSESSMENT OF ENVIRONMENTAL IMPACT.

Hans van der Sloot, Hans Meeussen*, Joris Dijkstra*,
Rob Comans*, Paul Seignette*, Ole Hjelmar**, David Kosson****

* ECN, Environmental Impact Assessment Group, The Netherlands

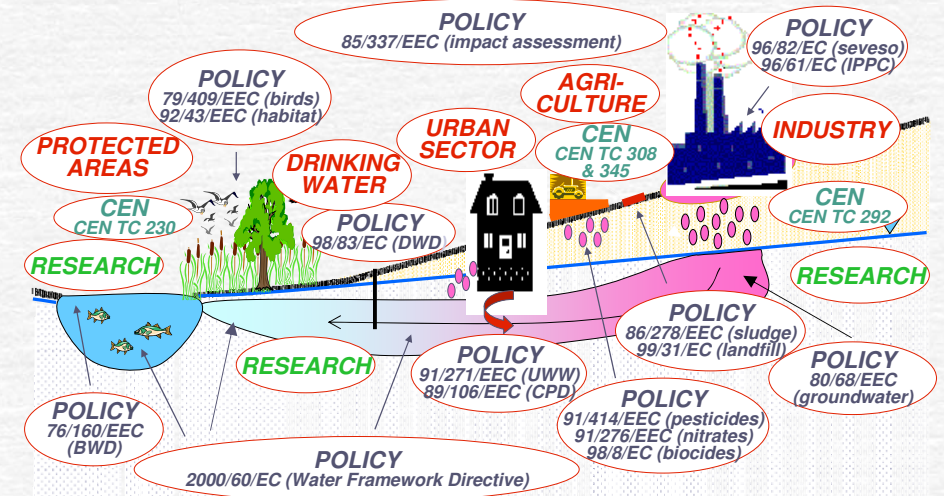
** DHI Water & Environment, Hørsholm, Denmark

*** Vanderbilt University, Nashville, USA

Workshop Source term October 19, 2006, Paris - France



Existing policy framework with many sources



From a presentation by Philippe Quevauviller at a CEN Workshop on 25-3-2006, Coimbra - Portugal



The way towards a solution

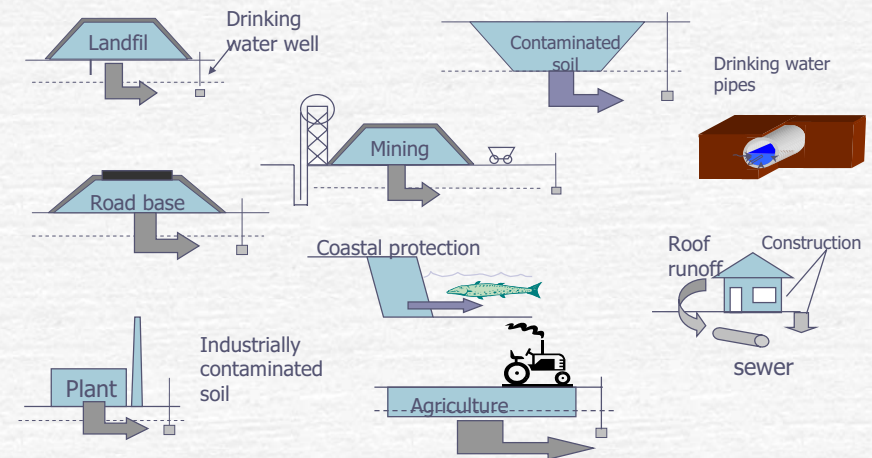
➤ Growing realisation on the part of regulators and researchers dealing with environmental issues

- Development of independent regulations for a wide range of different sectors is not an efficient approach to ensuring sustainable development.
- Material characterisation should provide the basis for decisions on the management of a material for any purpose
- Impact to soil and groundwater from different sources should be based on the same quality objectives.
- Goals can only be achieved through a more integrated and unified approach to impact evaluation.

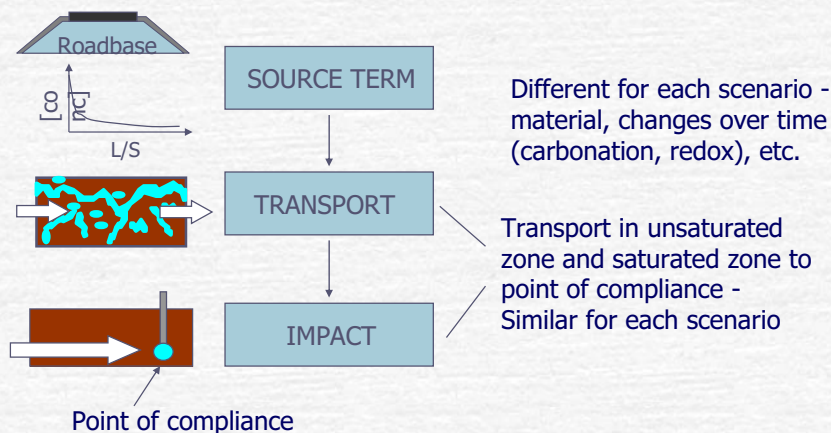


DIFFERENT IMPACT SCENARIOS.....

16 Dec. 2003
DG ENV



..... SIMILAR PROBLEM



Problems related to defining a source term

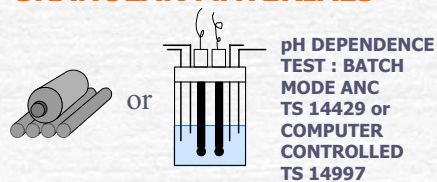
- Application of a constant source term in impact modelling
- Often a too limited set of constituents is taken along in the chemical reaction transport modelling
- Organic matter interaction, redox changes, gas reactions (volatility, carbonation and oxidation), pH changes are often not considered.
- Independent release functions are applied for individual constituents
- By far the majority of soil and groundwater impact models apply a K_d type of interaction to describe coupled reaction and transport.

The challenge: follow a full mechanistic approach taking into account mineral solubility, sorption to Fe and Al oxides, interaction with dissolved and organic matter, incorporation in solid solutions, changes in pH and redox as a result of atmospheric exposure, biological degradation or biologically mediated conversion, physical aspects such as particle size, permeability, preferential flow aspects, organic matter degradation and gas intrusion under varying degrees of saturation.



CHARACTERISATION LEACHING TESTS

GRANULAR MATERIALS

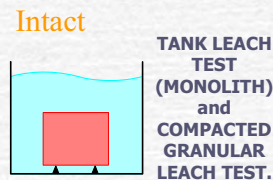
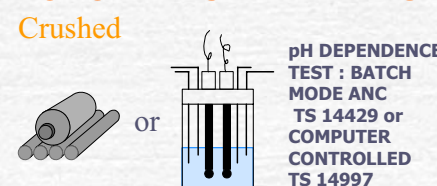


PERCOLATION LEACHING TEST (TS 14405)

EN 12920



MONOLITHIC MATERIALS



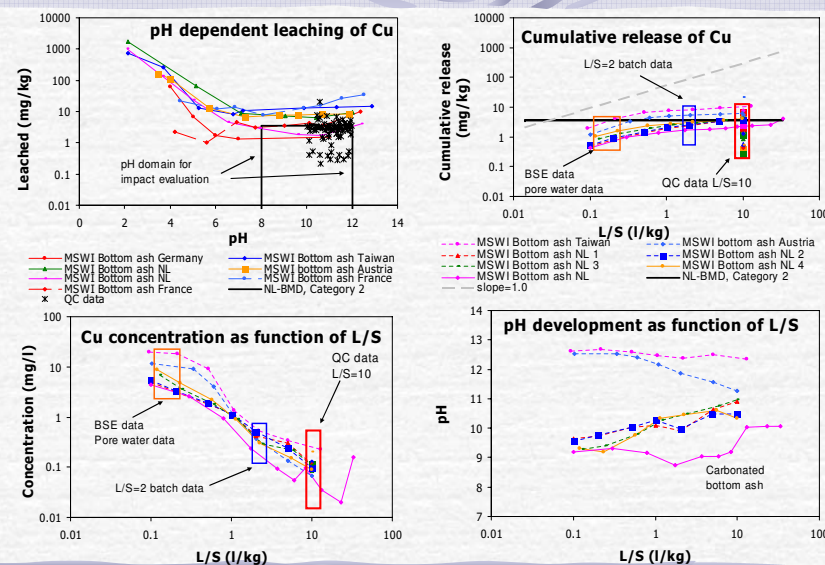
Chemical speciation aspects

Time dependent release

CEN/TC292, ISO TC190, CEN/TC345, CEN/TC351, CEN/TC223, SW846



INTEGRATED EVALUATION OF GRANULAR MATERIALS



ASPECTS COVERED IN THE INTEGRATED APPROACH

- Leaching behaviour in different exposure conditions in terms of pH (can be superimposed with redox status)
- Leaching behaviour as a function of time (through L/S)
- Consistency in outcome between different test
- Comparison of materials from other countries
- Comparison with regulation for the relevant exposure conditions (pH window; L/S range)
- Comparison of characterisation and compliance procedures
- Assessment of porewater concentrations in a field scenario
- Identification of release controlling mechanisms
- Starting information for geochemical modelling
- Evaluation of treatment options



STEPS IN CHEMICAL SPECIATION MODELING

- pH dependence leaching test on granular material or size reduced monolithic material for chemical speciation purposes
- measurement of release from granular materials in a percolation test or from monolithic specimen according to a type of tank test
- speciation modelling using LeachXS, a database-coupled version of the modelling environment ORCHESTRA, to identify relevant mineral phases (SI-indices)
- refined prediction of leaching behaviour in a pH dependence test based on the selected minerals and other relevant phases (Fe, Al, DOC, etc) providing a chemical speciation fingerprint
- this resulting speciation is used as input for the chemical reaction/transport modelling to describe the release from a percolation test or from a monolithic specimen (tank test simulation)
- model the field scenario with external factors (carbonation, oxidation, biologically mediated reactions) and realistic estimates of infiltration.



INPUT FOR CHEMICAL SPECIATION MODELLING

Production case
Speciation version
Material

Input specification
MSWI BA Austria + Iceland
MSWI BA Austria + Iceland
MSWI Bottom ash Austria

Selected fraction DOC
Sum of pH and pH
L/S
Clay
HFA
GFA

13.00
10.0000
0.000E+00 kg/kg
5.100E-03 kg/kg
0.000E-03 kg/kg

DOC (HA) data

pH

DOC (kg)

HA fraction

DOC (kg)

Polynomial coefficients

C0

C1

C2

C3

C4

C5

C6

C7

C8

C9

C10

C11

C12

C13

C14

C15

C16

C17

C18

C19

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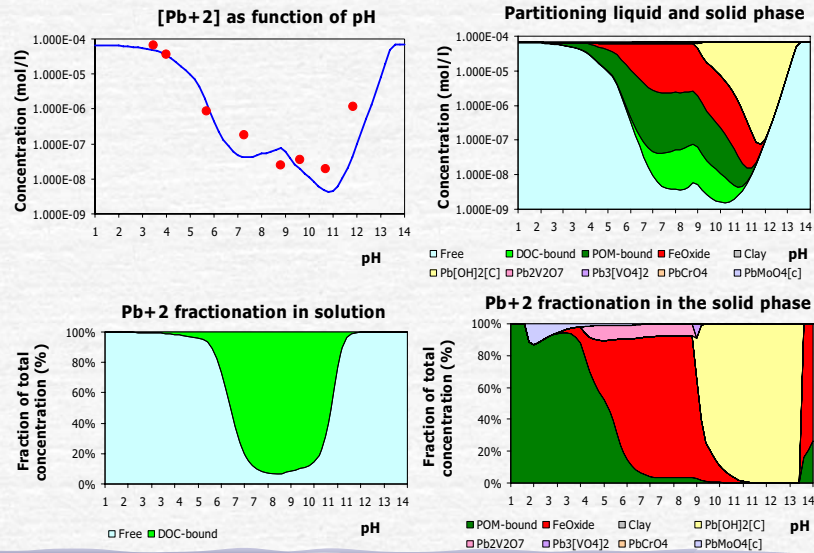
C263

C264

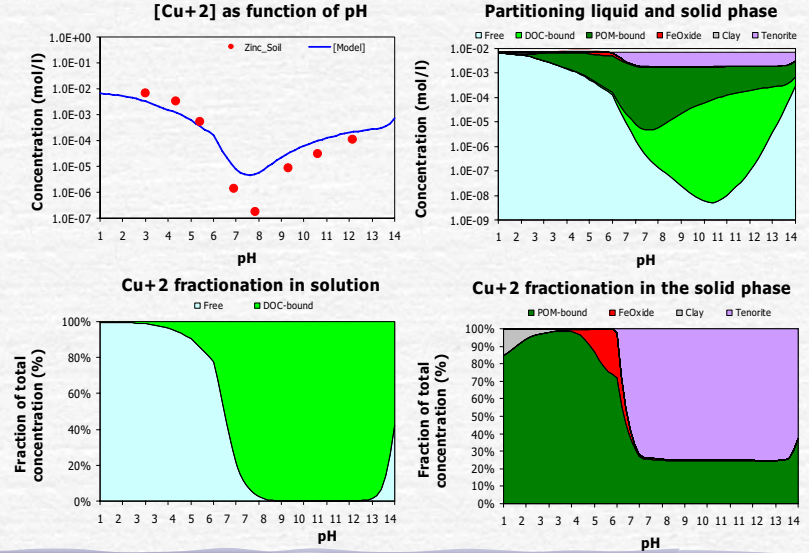
C265

C266

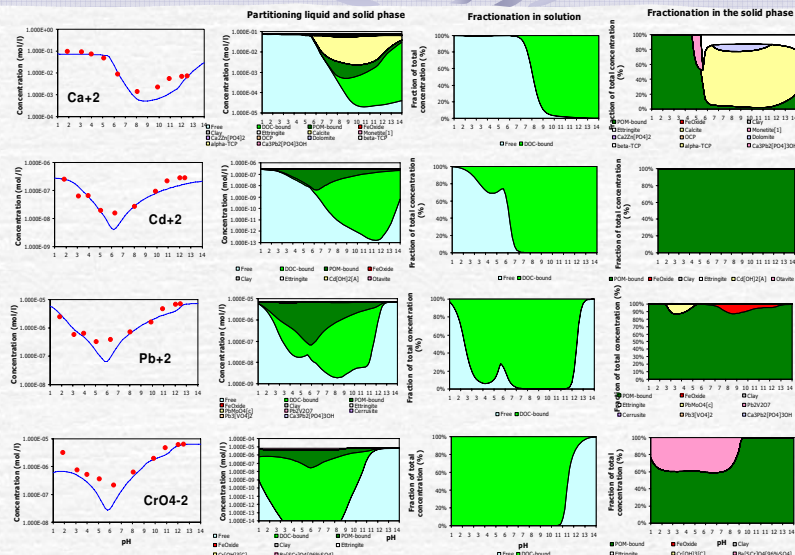
PARTITIONING FOR Pb in MSWI bottom ash



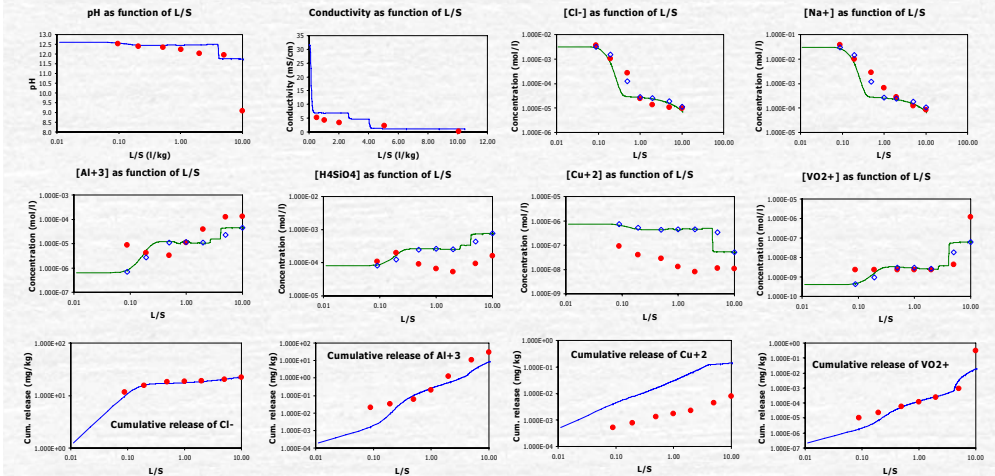
PARTITIONING FOR Cu in Zn-contaminated soil



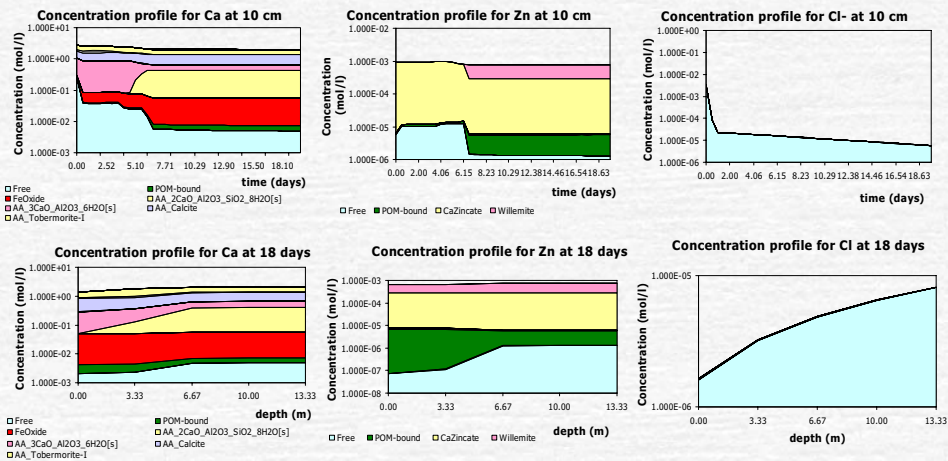
PARTITIONING FOR Ca, Cd, Pb and Cr in Compost



PREDICTION OF RELEASE IN PERCOLATION TEST FOR COAL FLY ASH



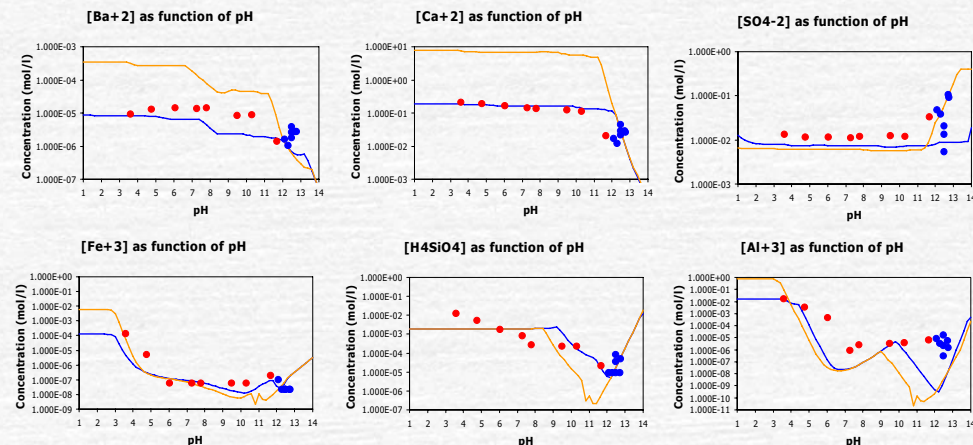
PARTITIONING IN A COAL FLY ASH COLUMN FOR Ca, Zn and Cl



Animation



RECENT IMPROVEMENTS



Simultaneously modelling release as a function of pH and release at low L/S to capture relevant mineral phases



Scenario Database (in preparation)

- road construction sub-base and embankments
- landfill
- monolithic waste landfill
- drinking water pipes
- treated wood construction
- multilayer applications
- oxidation of mining waste and slag
- monolithic structures
- prediction of release from material mixtures (blended cements, soil-fertiliser, soil-soil improver and mixed wastes)



Conclusions

- The characterisation leaching test methods developed in CEN/TC 292 for waste and ISO/TC 190 Soil are equally applicable to a wide range of other materials such as construction products and treated wood (horizontal standardisation). Similar methods adopted in SW 846 (US EPA)
- An integrated approach of assessing environmental impact for broad range of materials and products is the way to proceed and will help to avoid unnecessary duplication of work.
- Characterisation as described here will provide better understanding of material behaviour and partitioning and thus provide means to find solutions to
 - improvement of environmental quality,
 - a proper source term for impact evaluation in different exposure scenarios,
 - reference behaviour for typical materials
 - bioavailability and
 - allow placement of other (more limited) test data in perspective.



Conclusions

- Recent publications already provide a substantial part of the ruggedness testing needed to validate the characterisation methods. Financial support from European and international sources could be very cost effective in providing a sound reference base to more limited compliance testing.
- The chemical speciation fingerprint derived from the pH dependence test provides a chemical speciation fingerprint suitable for prediction of different laboratory test results, more complex impact modelling, evaluation of material mixes and a basis for assessing multilayer scenarios.
- The modelling work stresses the need for minor adjustments in the testing protocols and the need for additional parameters to be assessed - DOC fractionation, quantification of Fe and Al sorptive surfaces. It highlights missing mineral phases.
- The insight in release controlling processes provides better means to derive optimal compliance test procedures. Placing compliance test data in conjunction with characterisation data allows more far reaching conclusions.



Conclusions

- The full mechanistic modelling approach presented here is an ambitious approach, but given the current software capabilities it definitely seems the best way forward to environmental impact modelling of the wide variety of materials potentially affecting the atmosphere, soil, ground and surfacewater.
- Further development will be focused on building new scenarios and the verification of field observations against model predictions.



INFORMATION ON LEACHING AVAILABLE AT:

LEACHING BACKGROUND

www.leaching.net (Wascon 2003 workshop Leaching)

CONSTRUCTION PRODUCTS DIRECTIVE

www.cenorm.be/cenorm/workarea/sectorfora/construction+sector+network/conference.asp (CEN Workshop)

Report ECN-C--05-45 and ECN-C--04-060

LEACHING IN PROJECT HORIZONTAL

www.ecn.nl/horizontal (Desk study 23)

GRACOS EU project on contaminated soil and sediment

www.uni-tuebingen.de/gracos (Guideline)



Additional Background Slides



pH DEPENDENCE TEST

pH DEPENDENCE TEST TO ASSESS SENSITIVITY TO CHANGES IN pH - pH stat and "ANC" mode

TEST CONDITIONS **ANC MODE:**

BATCH TEST

8 FINAL pH VALUES (pH 4-12)

LEACHANT: PREDETERMINED AMOUNTS OF ACID OR BASE

LIQUID TO SOLID RATIO (L/S) = 10

RESULTS IN mg/l (GEOCHEMICAL MODELLING) OR mg/kg (RELEASE EVALUATION)

Scenario
Description

Material
characterization

Controlling
factors

Modelling
leaching

Validation
verification

Evaluation

Conclusions



pH DEPENDENCE TEST TO ASSESS SENSITIVITY TO CHANGES IN pH, E_H AND TEMPERATURE

(PrEn14429 Batch mode test)



CEN/TC 292 -
EN 12920

Scenario
Description

Material
characterization

Controlling
factors

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leaching

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verification

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Conclusions



ADVANTAGES OF pH DEPENDENCE TEST

- Identification of sensitivity of leaching to small pH changes
- Provides information on pH conditions imposed by external influences
- Basis for comparison of international leaching tests
- Basis for geochemical speciation modelling
- Provides acid neutralization capacity information
- Mutual comparison of widely different materials to assess similarities in leaching behaviour
- Recognition of factors controlling release
- For non-interacting species possible to assess sub-sampling error

Applicable to almost any material



PERCOLATION TEST TO ASSESS LONG TERM RELEASE FOR GRANULAR MATERIALS TS 14405

Liquid to solid ratio (L/S) related to a time scale by infiltration rate, density and height of application.

TEST CONDITIONS:

Pre-equilibration after saturation for more than 48 hrs

Up-flow

L/S range 0.1 - 10 (100 - 1000 yrs)

Test data in mg/l or mg/kg cumulative



CEN/TC 292 -
EN 12920

Scenario
Description

Material
characterization

Controlling
factors

Modelling
leaching

Validation
verification

Evaluation

Conclusions



ADVANTAGES OF PERCOLATION TEST

- Identification of solubility control versus wash out
- Indication of pore water concentrations relevant to field leachate from low L/S data
- Local equilibrium established quite rapidly
- Basis for geochemical speciation modelling
- Allows comparison with lysimeter and field data provided L/S value can be obtained from such measurements
- Projection towards long term behaviour possible
 - Solubility controlled release
 - Wash-out of non-interacting species

Applicable to many materials. Limited or not applicable to clayey soils and sediments (low permeability)



TANK LEACH TEST OR COMPACTED GRANULAR LEACH TEST (CGLT) FOR MONOLITHIC MATERIALS (modified)

TEST CONDITIONS:

First step: pre-equilibration

for 48 hrs at liquid to

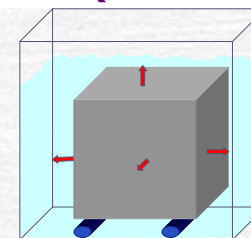
volume ratio: 5

Second step: leaching

at low L/V ratio (1) for 24 hrs

Then contact times: 2, 4, 8, 16, 32 and 64 days

Leachant: demineralised water (own pH)



Expression of results in mg/m^2 (cumulative) against time



CEN/TC 292 -
EN 12920

Scenario
Description

Material
characterization

Controlling
factors

Modelling
leaching

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verification

Evaluation

Conclusions

EXPERIMENTAL SET-UP



CGLT = Compacted Granular Leach Test



ADVANTAGES OF TANK LEACHING TEST OR COMPACTED GRANULAR LEACH TEST

- Relevant for materials with monolithic character (durable materials) or materials behaving as monolith (low permeability soil and sediments)
- Identification of solubility control versus dynamic leaching possible
- Isolation of surface wash-off effects
- Quantification of intrinsic release parameters
- Basis for reactive/transport modelling
- Projection towards long term behaviour possible

Applicable to sediments, clayey soils, stabilised materials and construction materials produced



Re-use of waste and behaviour of heavy metals : a molecular approach of the transfer mechanisms

J. Rose^{1,2}, J-Y Bottero^{1,2},
P. Chaurand^{1,2}, A. Bénard^{2,3}, J. Domas^{2,3}, J. Susini⁴, A-M
Flank⁵, D. Borschneck¹, L. Trotignon⁶, J-L Hazemann⁷,
D. François⁸, L. De-Windt⁹

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PSME 112, Europole Méditerranéen de l'Arbois, BP80, 13545 Aix en Provence Cedex 4, France.

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France

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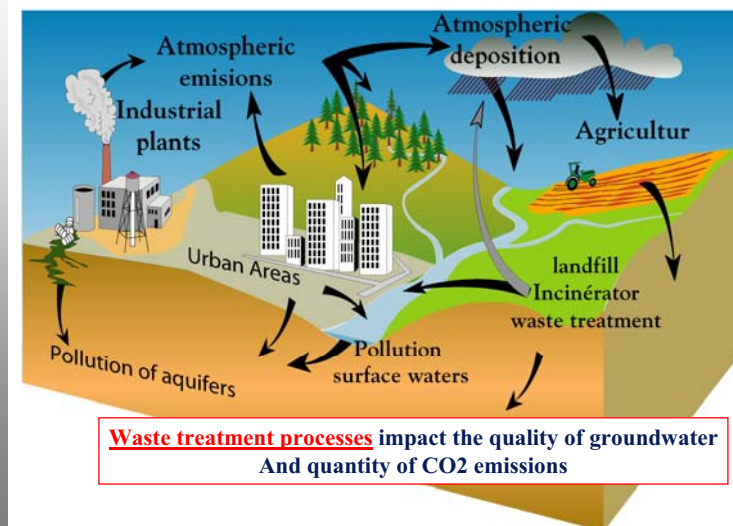
⁷Laboratoire de Cristallographie-Bp166. 38042 Grenoble. Cedex9 France

⁸LCPC Route de Bouaye, BP 4129 44341 BOUGUENNAIS Cedex FRANCE

⁹Centre de Géosciences - Ecole des Mines de Paris, 77305 Fontainebleau cedex (France)

October 19-20, 2006 Paris

Environmental effects of human activities (pollutant transfer, toxicity...)



Case of solid and liquid waste containing heavy metals.

- Mechanistic approach...(not always the more efficient)
- Speciation of metals and metalloïds within the source term : atomic environment and redox state: affects mobility and toxicity

A lot of examples: Cr^{III}/Cr^{VI}, V^{III}/V^{IV}/V^V, As^{III}/As^V,

Inorganic v.s organic form: **Toxicity**
AsH₃>As(-III)>As(III)>As(V)>As-organic

Case of solid and liquid waste containing heavy metals.

Table 1. Relation between metal concentration,
solubility, and toxicity.

Compound	Toxicity upon ingestion (mg / kg)	Solubility	[Co]
Cobalt	> 7000	2 mg/l	100%
Co oxide	> 5000	8 µg/l	71%
Co sulfate	768	60 g/l	22%
Co chloride	766	76 g/l	24%
Co nitrate	691	240 g/l	20%
Co acetate	503	237 g/l	23%

Speciation in the solid phase

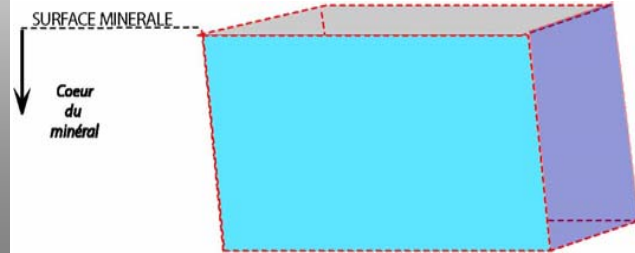
■ Presence of a metallic phase

Table 1. Relation between metal concentration, solubility, and toxicity.

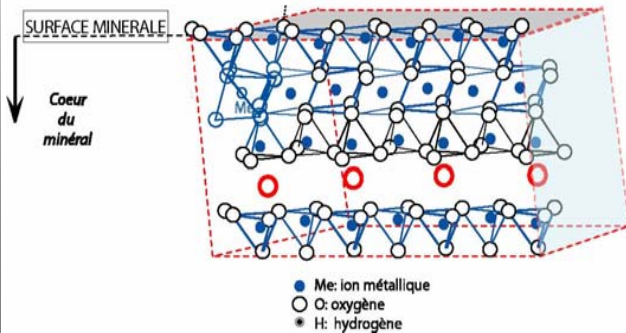
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Speciation in the solid phase

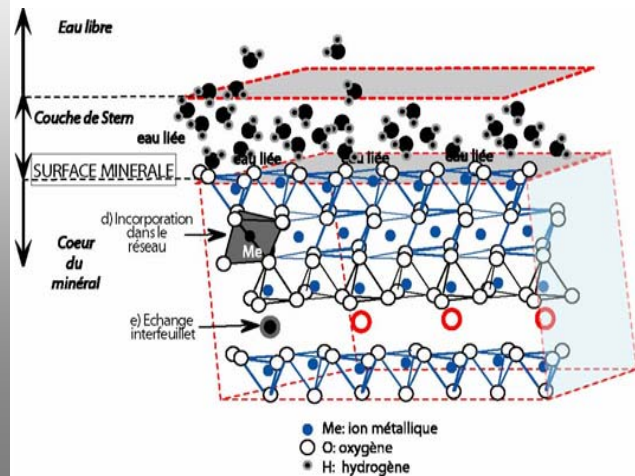
■ No metallic phase : more complex



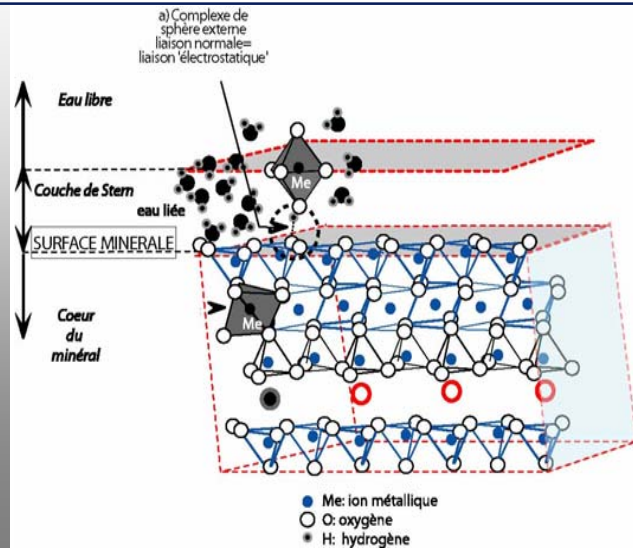
Speciation in the solid phase



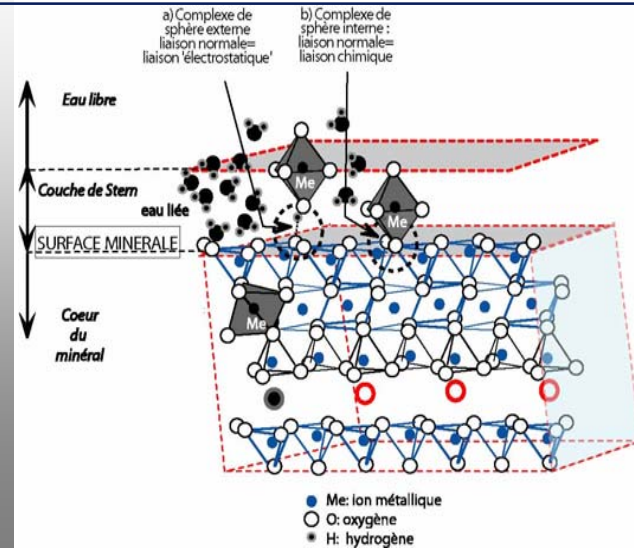
Speciation in the solid phase



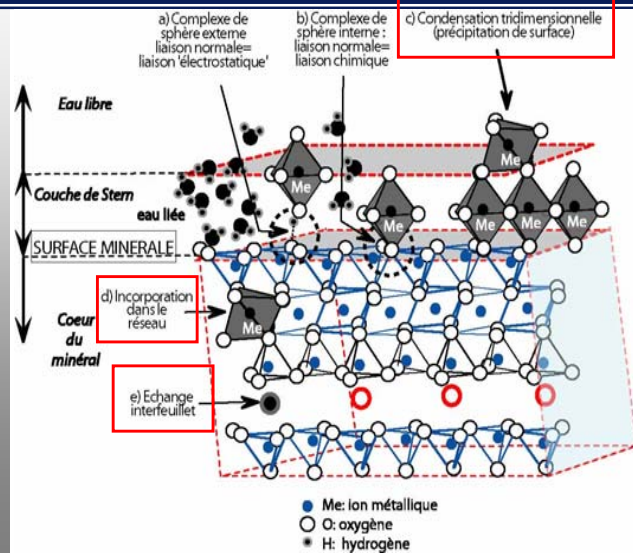
Speciation in the solid phase



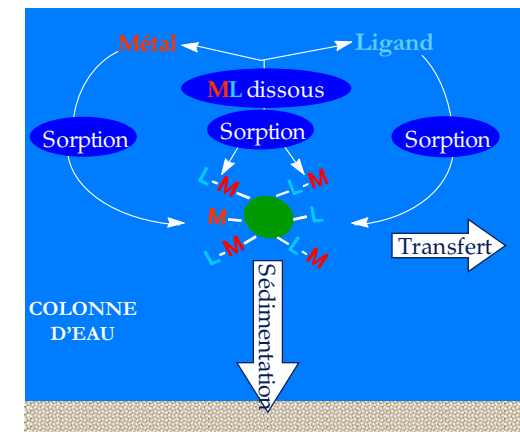
Speciation in the solid phase



Speciation in the solid phase

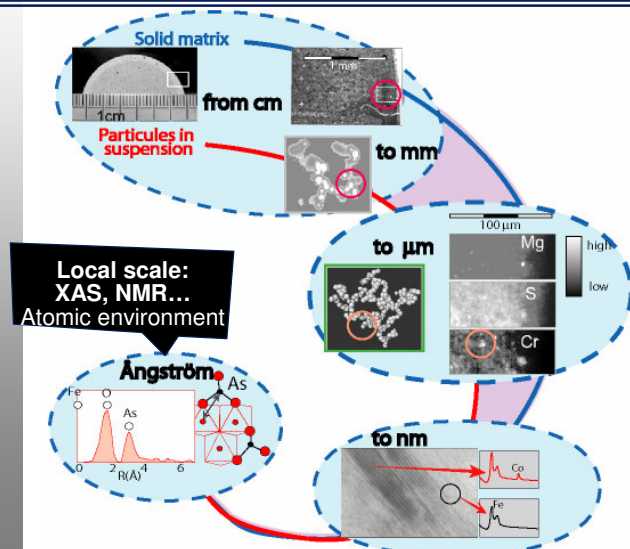


Speciation in the liquid phase



But generally sludge...

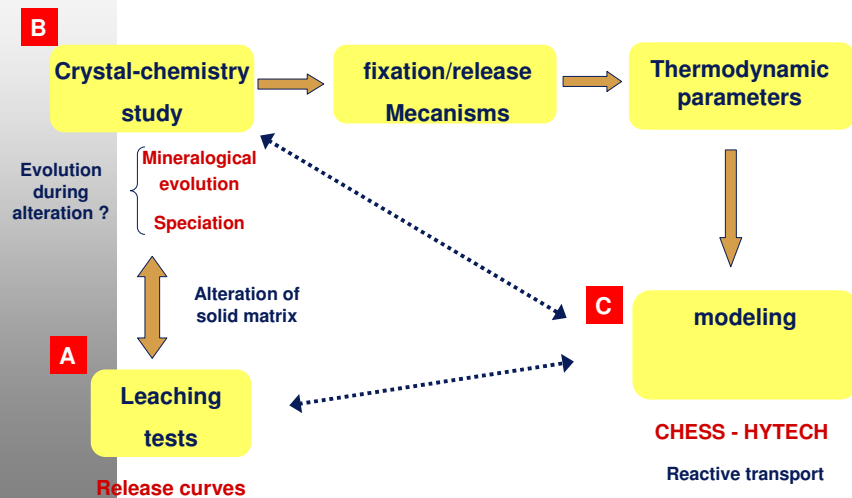
Multi-scale structural study



Synchrotron

QuickTime™ et un
décompresseur
sont requis pour visionner cette image.

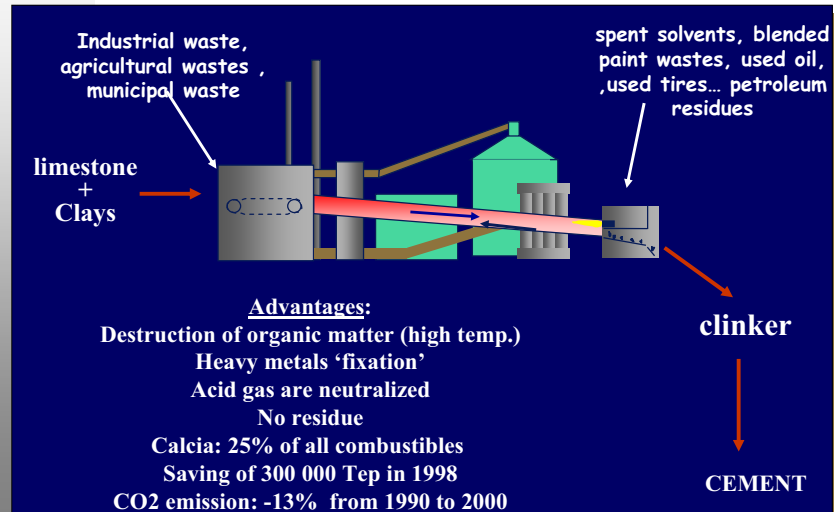
Speciation : not enough...



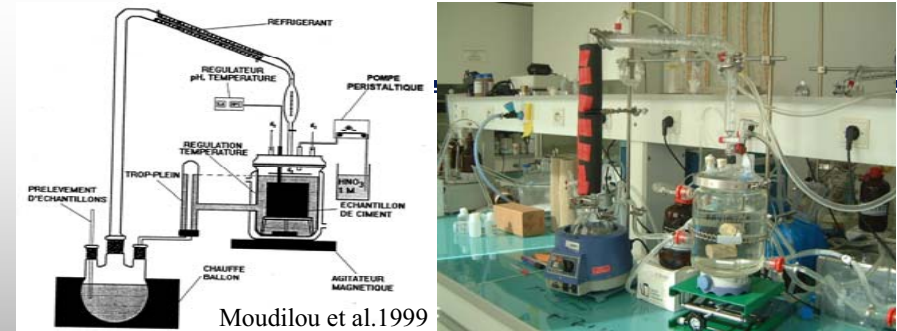
Some examples

- Cr(VI) in cement phases (waste co-firing)...(before Fe(II) treatment)
- Cr and V in BOF Steel slag (reuse in road making)

Alternative fuel - co-firing



Experimental conditions



1.65 cm
4.5 cm

1 CEM I
1 CEM III/A

L/S = 0.5
28 days
Cr⁶ or Cr³
0-2000 ppm

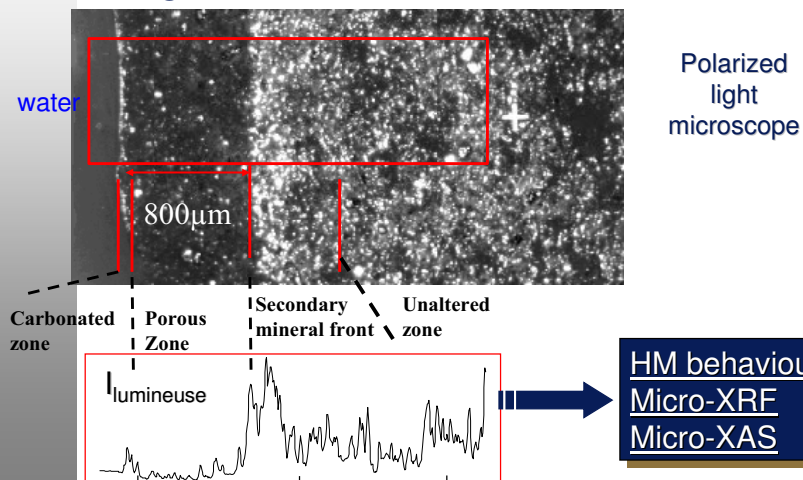
Leaching: 42 days pH = 5 température 40°C

Analyses: liquids and solids

Moudilou, E.; Bellotto, M.; Defosse, C.; Serclerat, Y.;
Baillif, P.; Touray, J. C. Waste Manage. 2002, 22, 153-157.

High spatial heterogeneity: chemical, mineralogical, textural: importance of imaging techniques

Image of the surface of altered cements



Chromium behaviour during leaching

Case of Cr:

Cr(VI)-Cr(III):
Cr(VI) is more soluble (and toxic) and should be released. Cr(VI) should be absent in the altered layer after the ettringite front? (predicted by models)

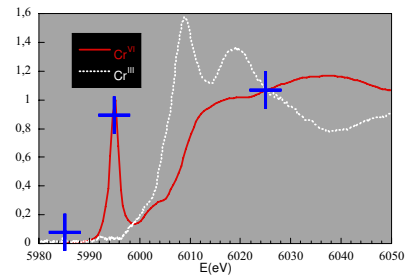
Prediction: analysis of the solid matrix is needed

Chromium behaviour during leaching

μ -XANES- μ -SXRf (ESRF)

- Beam size : $1 \times 1 \mu\text{m}$
- Detection limit : few 10 ppm
- Enable speciation of Cr

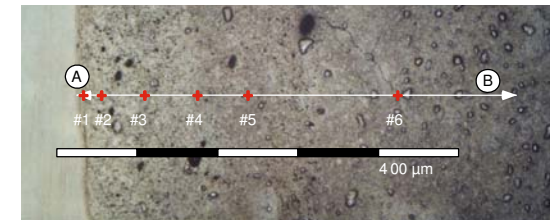
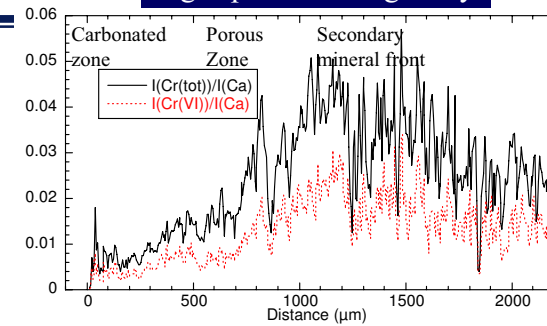
ID 21 Beamline ESRF-
Grenoble France



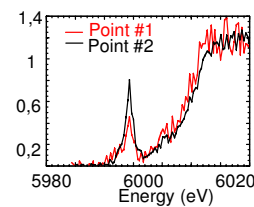
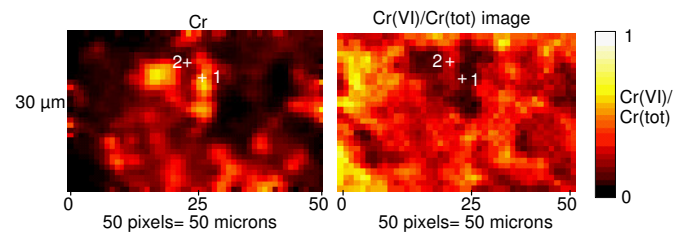
Surface
layer

Cr (tot) and Cr(VI) line scans high spatial heterogeneity

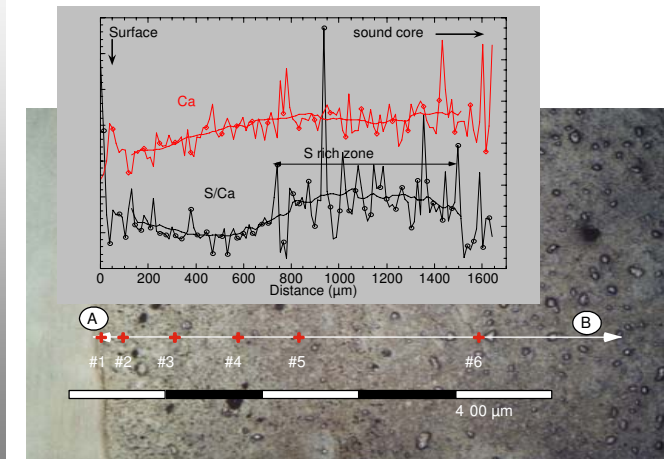
Unaltered
zone



Cr (tot) and Cr(VI) images: high spatial heterogeneity

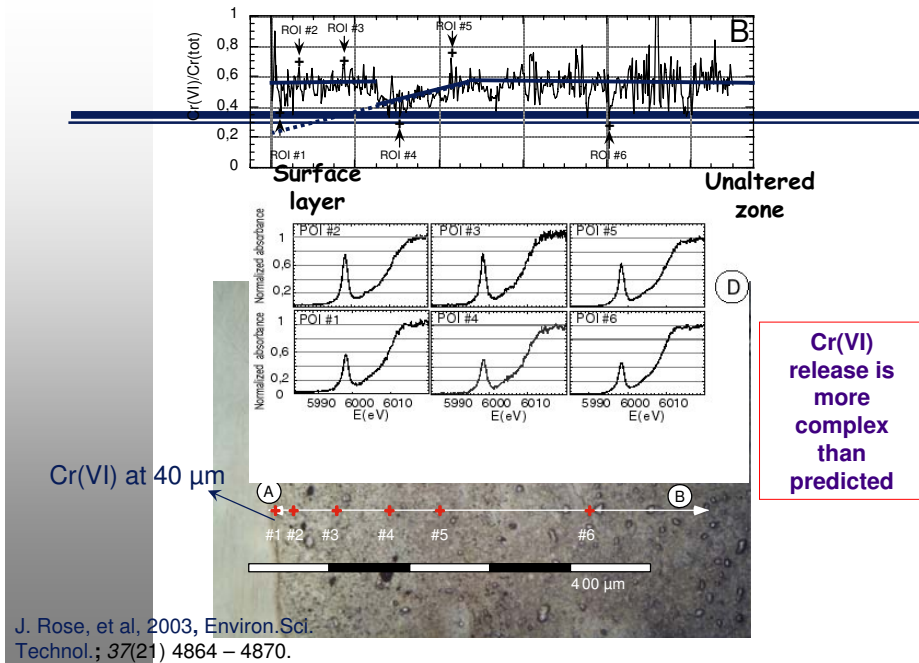


Cr accumulation front: ettringite front



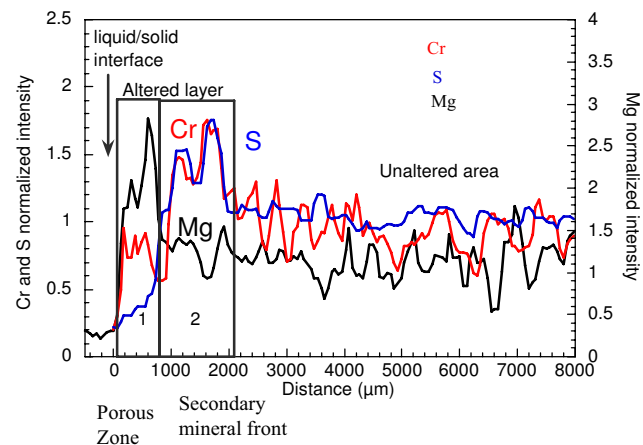
Chromium behaviour

- Cr(VI) less mobile than predicted by models.
- Which mineral can fix Cr(VI) ?



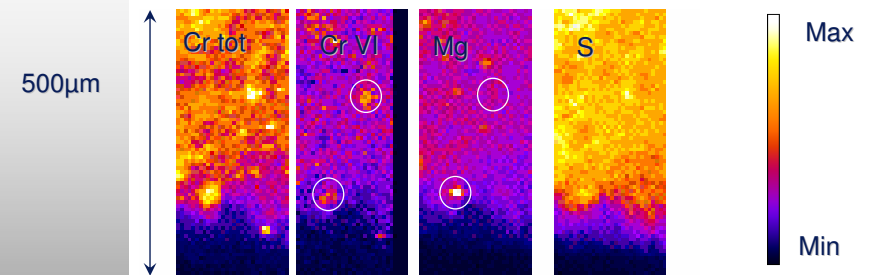
Cr(VI) release is more complex than predicted

μ-XRF



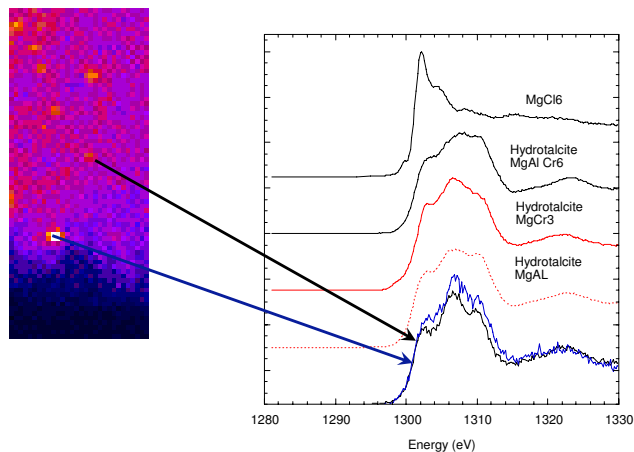
μ-XANES

LUCIA beamline
SLS-Villigen



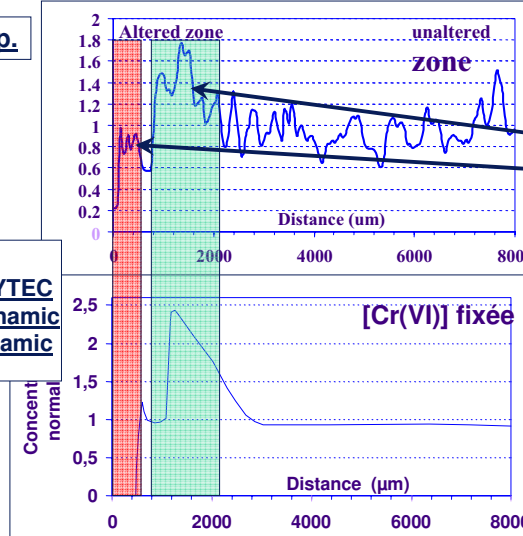
Cr and Mg are correlated in the altered layer

Mg K edge XANES



Porous Zone Secondary mineral front

Exp.



Ettringite and hydrotalcite

Ph'D A. Benard

Model
CHESS+HYTEC
Thermodynamic
+hydrodynamic

1. Context and objectives of the study

Environmental impact of waste reuse:
Cr and V in BOF steel slag

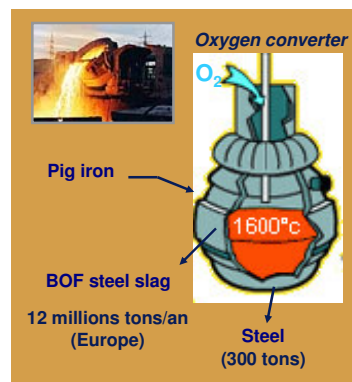
Definition of
BOF slag

❖ **Basic Oxygen Furnace (BOF) slag** is a **residue** from the **converter** in steel-making operations.

❖ In Europe, a significant portion of BOF slag is **reused** as aggregates in **road constructions** (unbound layers).



Release of pollutants
Environmental impacts ?



1. Context and objectives of the study

Environmental impact of waste reuse

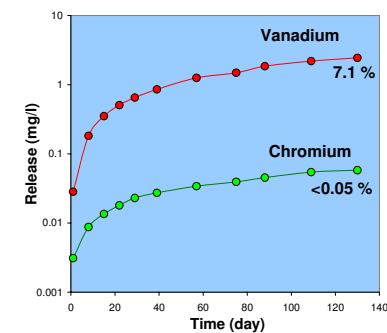
Traces elements
in BOF slag

❖ BOF slag contains trace amounts of **potential toxic** element which can be released : **Chromium** (Cr, 2400 mg/kg) and **Vanadium** (V, 690 mg/kg).

❖ **Dynamic leaching tests** at a laboratory scale (modified soxhlet extractor¹):

Leaching conditions

130 days, leachate = UPW,
pH = 8.5 – 9, L/S = 20,
recirculation flow = 5 ml/min.



❖ Objective: Explain **Cr and V leaching behavior** by identifying the **molecular release/retention mechanisms** associated.

❖ Final objective : **modeling** the **long-term behavior** of reused BOF slag.

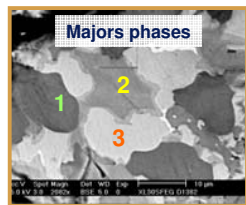
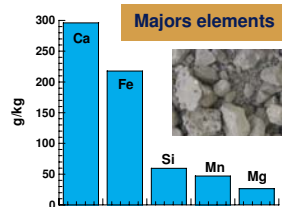
¹E. Moudilou et al., Waste Management 22(2), 153 (2002).

1. Context and objectives of the study

Environmental impact of waste reuse

Majors phases
in BOF slag

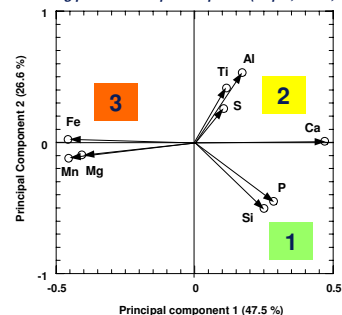
❖ BOF slag **solid matrix** was well defined by using complementary techniques:
ICP-AES, DRX, MEB-EDS, μ -XRF.



SEM photograph of a polished BOF slag section

1. $\text{Ca}_2\text{SiO}_4 + \text{P}$ (Iarnite)
2. $\text{Ca}_2\text{Fe}_{2-x}\text{AlO}_5$ (brownmillerite) + Ti, S
3. (Fe, Mn, Mg)O (solid solution, wustite)

PCA loading plot from 143 μ -XRF spectra (10 μm , 15 kV, 1000 s)



4. Results on V speciation

Chromium bearing phase

Techniques :
 μ -XRF
SIMPLISMA

Laboratory μ -XRF

(XGT⁵⁰⁰⁰, Horiba Jobin-Yvon)

μ -XRF spectrum : 10 μm spot size, 15 kV, 1000 s,
Rh X-ray target source, N = 145

SIMPLISMA approach: a chemometrics tool

Simple-to-use Interactive Self Modeling Mixture Analysis

Iterative Principal Component Analysis

❖ SIMPLISMA is a powerful chemometrics tool to elucidate XRF spectra that statistically explain the **variability from a data set of N μ -XRF spectra** (N=145).

❖ SIMPLISMA is based on the determination of “**pure variables**” (showing highest variation in their intensity) followed by the calculation of “**pure component spectra**” and their associated contributions.

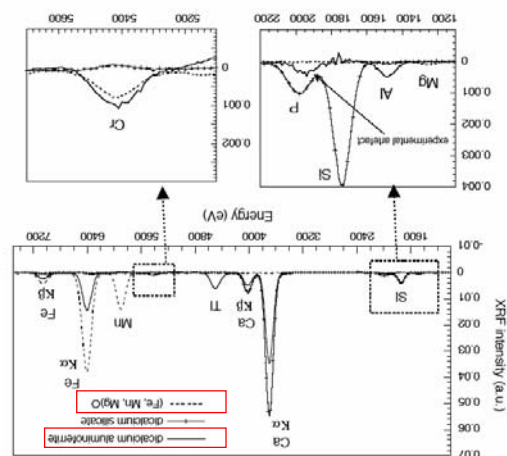
❖ The **Ti, Mn and Si fluorescence $K\alpha$ lines** were **interactively selected** as “pure variables”.

3. Results on Cr speciation

Chromium oxidation state

Techniques :
XANES
 μ -XANES

Initially only Cr(III) is present in BOF slag and no Cr(VI) is formed during leaching

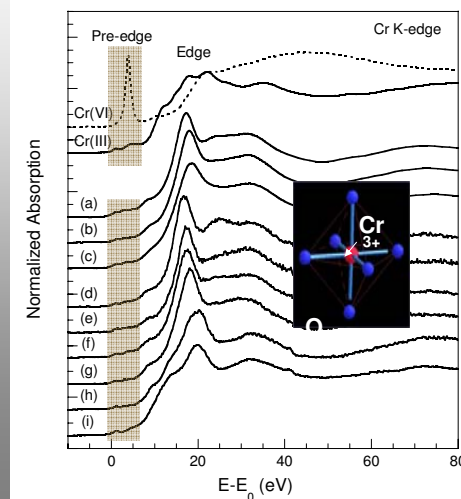


Bulk XANES

BOF slag non altered
Altered layer (2 years in lysimeter)
Altered layer (130 days in laboratory)

μ -XANES

Incident micro beam of
1*0.35 μm^2 pointed on Cr-rich
spots in altered and non-altered
regions (ID21, ESRF, France)



3. Results on Cr speciation

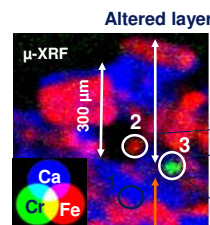
Chromium speciation under leaching conditions

Techniques :

μ -XRD

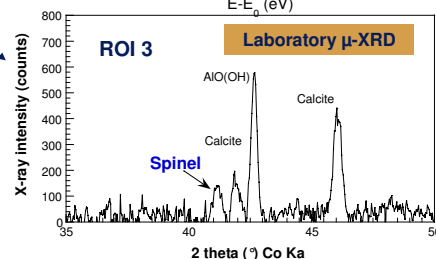
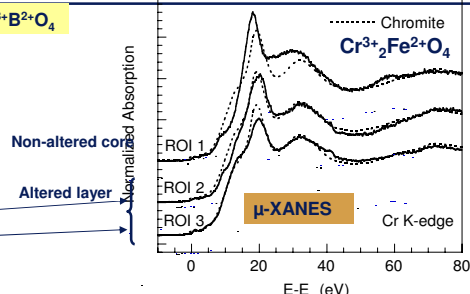
μ -XANES

Spinel-type phase : $A_2^{3+}B_2^{2+}O_4$



Non-altered core

(X'Pert Pro MPD, Panalytical)
100 μ m spot size



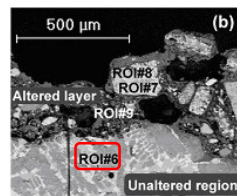
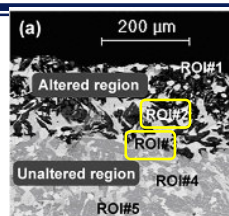
4. Results on V speciation

Vanadium oxidation state

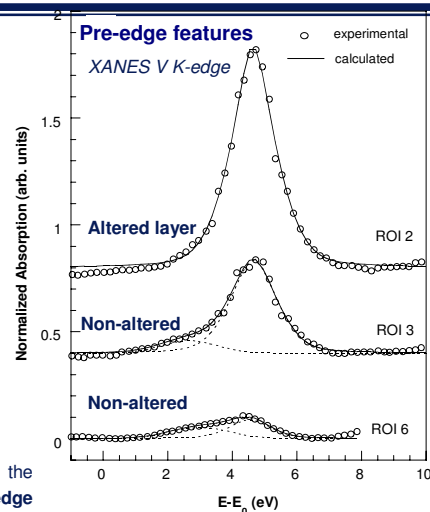
Techniques :

XANES and

μ -XANES



From the non-altered core to the altered layer : changes in the **pre-edge** peak position and intensity.



4. Results on V speciation

Environmental impact of waste reuse

❖ Initial V content = 690 mg/kg BOF slag. V total release is relatively high (7.1 % after 130 days of leaching)

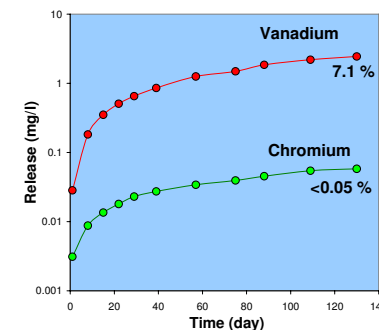
❖ As for Cr, V toxicity and mobility depends on its oxidation state.

- V(III) less toxic than V(IV) and V(V). V(V) is the most toxic form.

❖ Dynamic leaching tests at a laboratory scale (modified soxhlet extractor¹).

Leaching conditions

130 days, leachate = UPW,
pH = 8.5 – 9, L/S = 20,
recirculation flow = 5 ml/min.



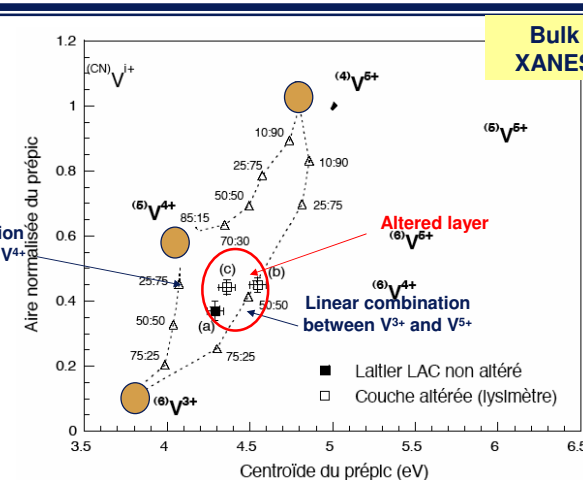
4. Results on V speciation

Vanadium oxidation state

Techniques :

XANES

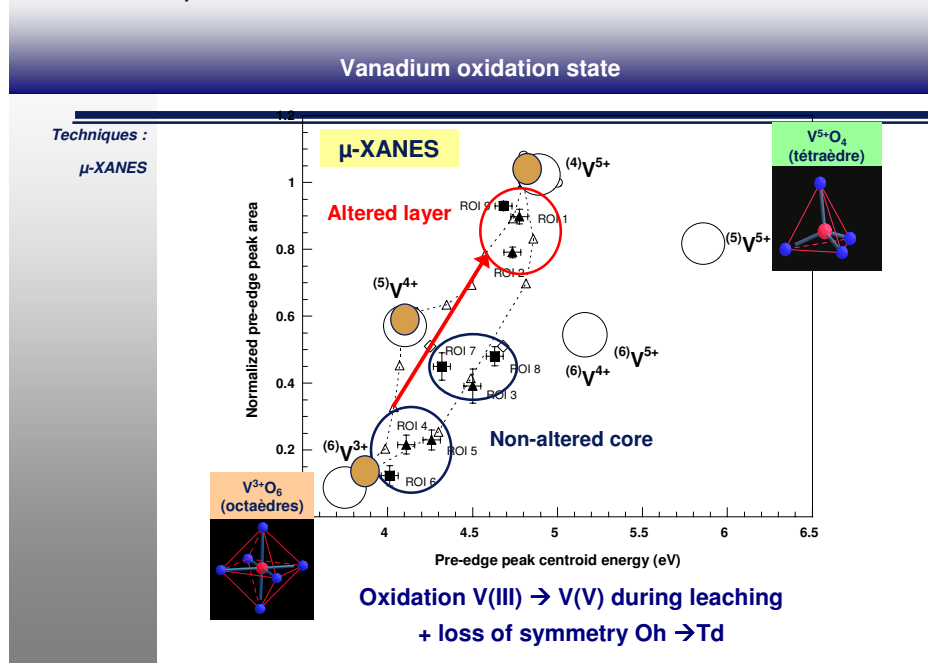
Linear combination between V³⁺ and V⁴⁺



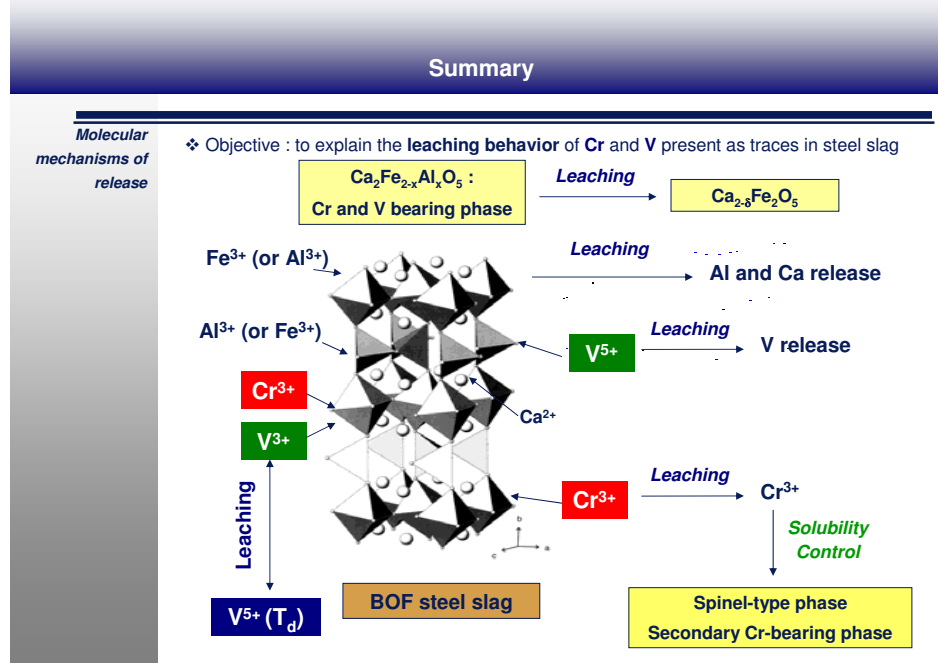
V in non-altered BOF slag : mixture between (6)V³⁺ and (4)V⁵⁺

Confirmed with EXAFS (V-O interatomic distances¹)

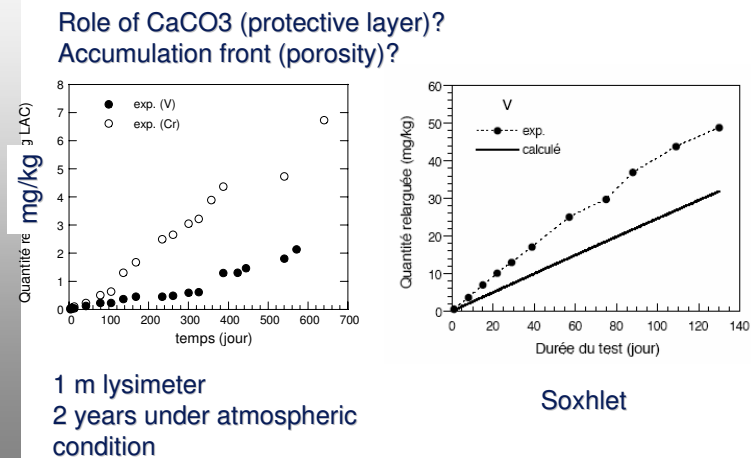
4. Results on V speciation



5. Conclusion



Out of the lab...

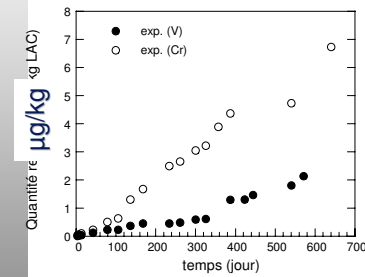


Conclusion - perspective

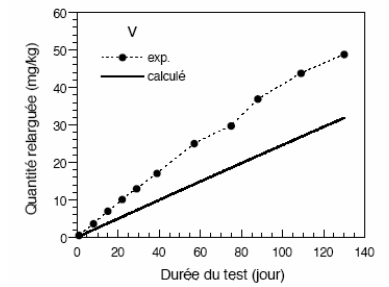
- Mechanistic approach can be performed at the molecular level
- Necessity of large scale leaching experiment
- Effect of organic matter and living organisms

Technological development...

- XRF scanner (beam resolution 200 μm) for large samples (1.8 m : cores from lysimeter...)
- Redox state for core samples (high energy resolution XRF (inelastic X-ray fluorescence))
- ...



1 m lysimeter



Soxhlet

Characterisation and modelling geochemical processes controlling the leaching of contaminated materials: a generic approach applied to MSWI bottom ash

Rob Comans, Joris Dijkstra, Andre van Zomeren, Hans Meeussen, Hans van der Sloot



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Outline

- ✓ Introduction
 - Research aim
 - General modelling approach
 - Major processes and parameters to be considered
- ✓ Modelling results & experimental verification
 - Batch pH-static leaching test TS14997
 - Percolation test TS 14405: variation of flow velocity and flow interruption
- ✓ Conclusions & future challenges

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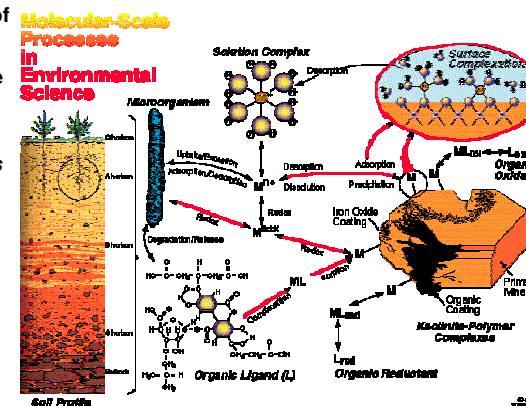
Introduction

- **Predictive models:**
 - indispensable tools in environmental risk assessment of contaminant source term
 - often developed for specific contaminated materials/situations: limited general applicability
- **Generally applicable models and standardised measurements for source term characterisation** required for development of consistent environmental protection strategy for utilisation of contaminated materials
- **Perspective:**
 - geochemical models based on thermodynamic parameters for fundamental processes controlling element speciation and mobility
 - Recent research: general geochemical principles control leaching and speciation of contaminants in many different materials
- **Starting point: Generic modelling approach feasible** when combined with consistent leaching/extraction methods based on same principles (i.e. major variables controlling contaminant speciation and mobility in source term)

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Types of geochemical processes to be considered

- **Dissolution and (re)precipitation of minerals/salts**
- **Adsorption/desorption on reactive mineral and organic surfaces in solid phase:**
 - Organic (humic) substances
 - Fe/Al-(hydr)oxides
 - Clay minerals
- **Complexation with soluble constituents (ligands):**
 - Inorganic (OH^- , HCO_3^- , Cl^- , etc.)
 - Organic (humic and fulvic acids)



Source: Surface and Aqueous Geochemistry Group, Stanford, USA
Source: Surface and Aqueous Geochemistry Group, Stanford, USA

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Characterisation leaching tests: pH-static and percolation test

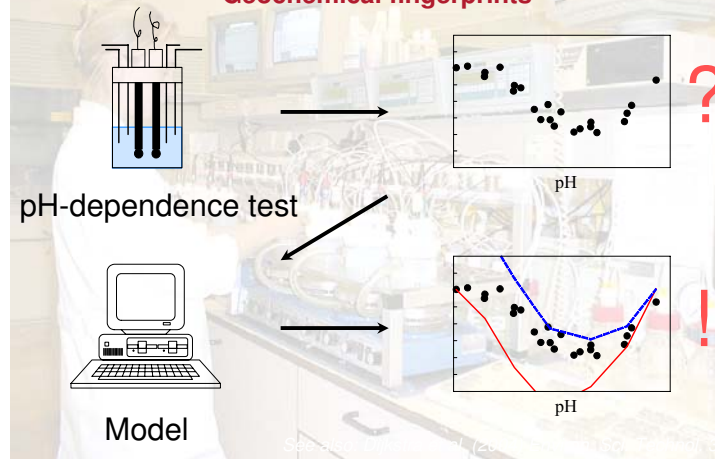


Automated pH-static (TS14997) and percolation (TS 14405) test

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Approach to identification of geochemical processes:

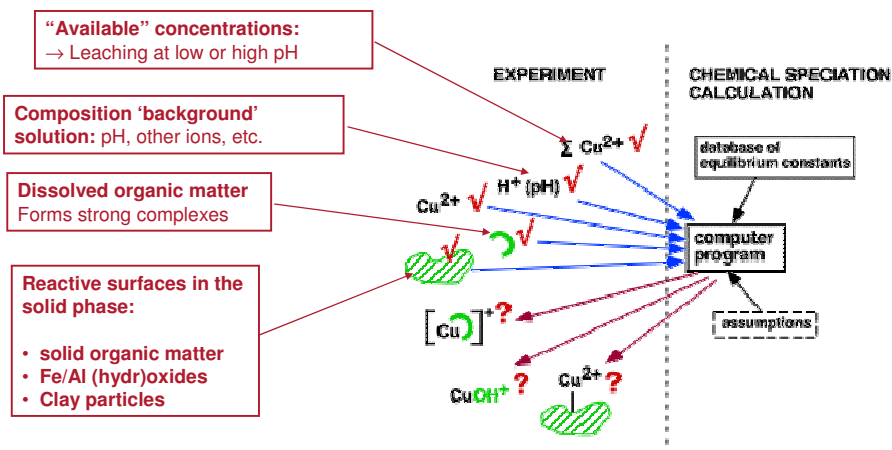
"Geochemical fingerprints"



See also: Dijkstra et al. (2004) *Environ. Sci. Technol.* 38, 4390-4395.

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Modelling leaching processes:



After M. Gfeller & R. Schulin, ETH, Zürich

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Modelling approach using Orchestra*

- Chemical speciation: *Minteq 4.0 database (NIST thermodynamic data)*.
- Dissolution and precipitation of minerals present in MSWI bottom ash
- (Sub-)models for adsorption to reactive surfaces
 - Fe/Al (hydr)oxides – GTLM (Dzombak & Morel, 1990), surface complexation/precipitation
 - Solid and dissolved humic substances – NICA-Donnan (Milne et al., 2003)
- Transport processes (convection, dispersion, diffusion, preferential flow, dual porosity)

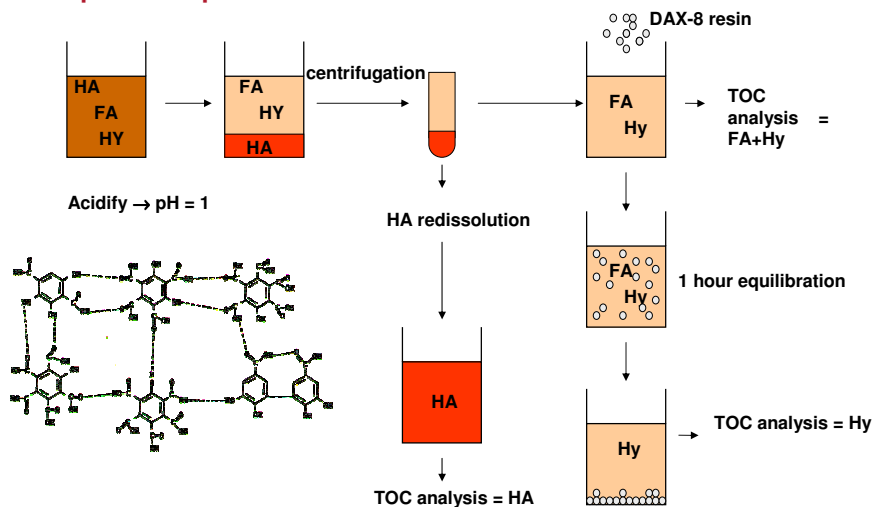
Parameterisation:

- 'Mechanistic' models, *no fitting* of parameters, 'predictive' approach
- Careful selection of plausible minerals/processes based on literature
- Independent measurements of input- parameters (selective extractions)
- Single set of parameters to predict *both* pH-dependence and percolation

*Meeussen, J.C.L., *Environ. Sci. Tech.* 37 (2003), 1175-1182

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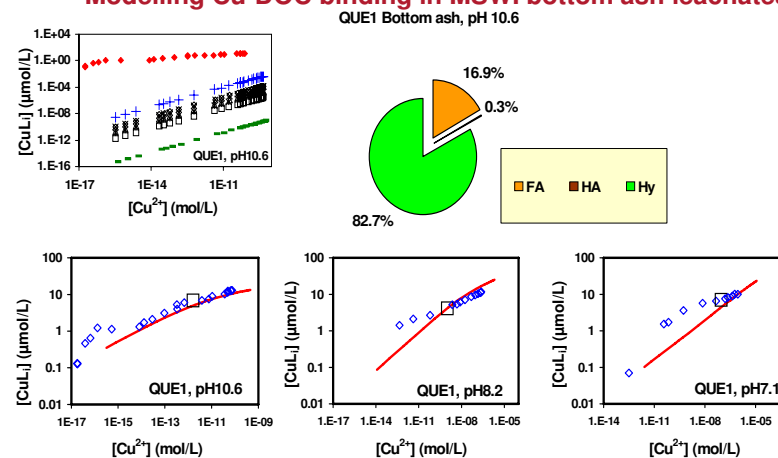
Rapid batch procedure for determination of humic and fulvic acids*



* van Zomeren & Comans, 2006 (submitted for publication)

www.ecn.nl

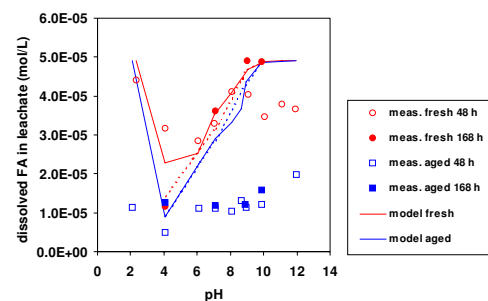
Modelling Cu-DOC binding in MSWI bottom ash leachates



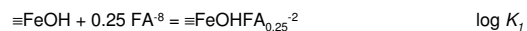
van Zomeren & Comans (2004) *Environ. Sci. Technol.* 38, 3927-3932

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Modelling pH-dependent leaching of fulvic acid



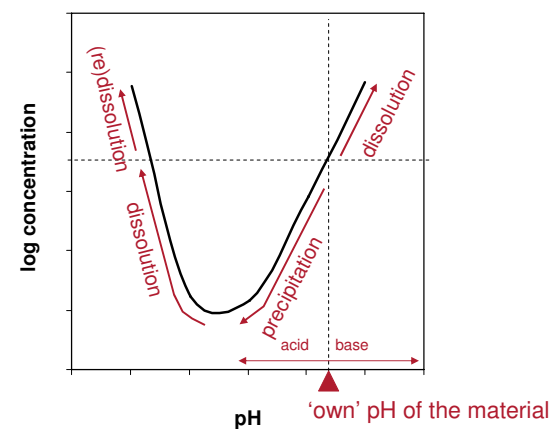
Surface complexation of FA on Fe(hydr)oxides:



Dijkstra J.J. et al., *Environmental Science and Technology* 40, 4481-4487 (2006).

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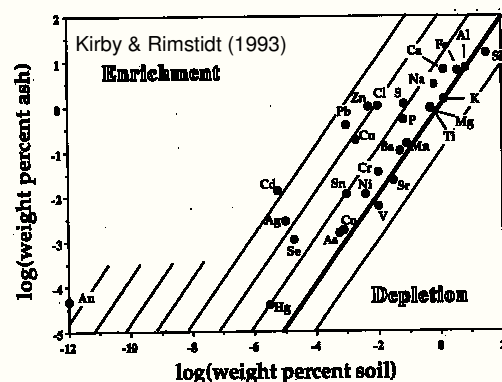
'kinetics' of leaching



Dijkstra et al., *Applied Geochemistry* 21 (2006) 335-351

www.ecn.nl

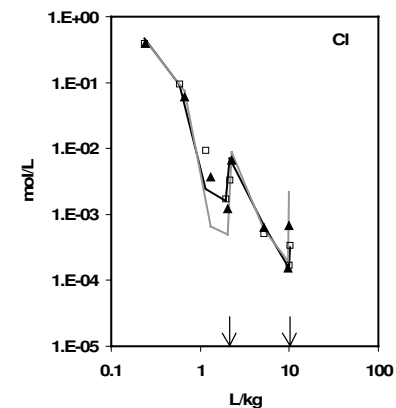
MSWI bottom ash



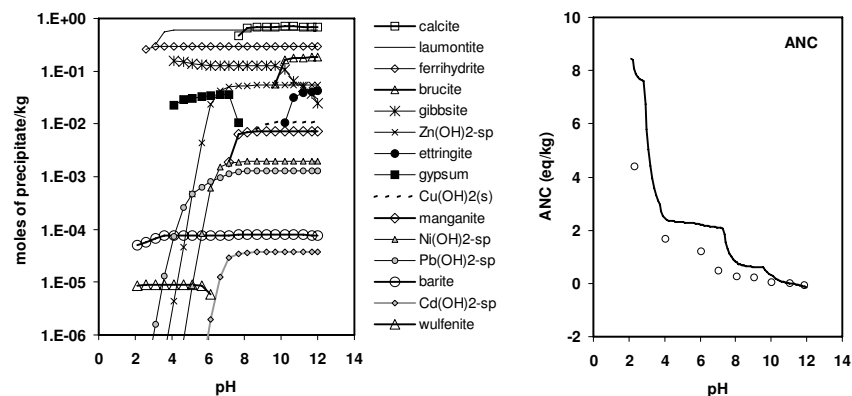
- Produced in large quantities in many countries
- Often beneficially utilised in construction (leaching limits)
- Source term enriched in many potential contaminants
- Solid/liquid partitioning of both heavy metals and oxyanions controlled by inorganic and organic reactive surfaces.

Characterisation of water flow

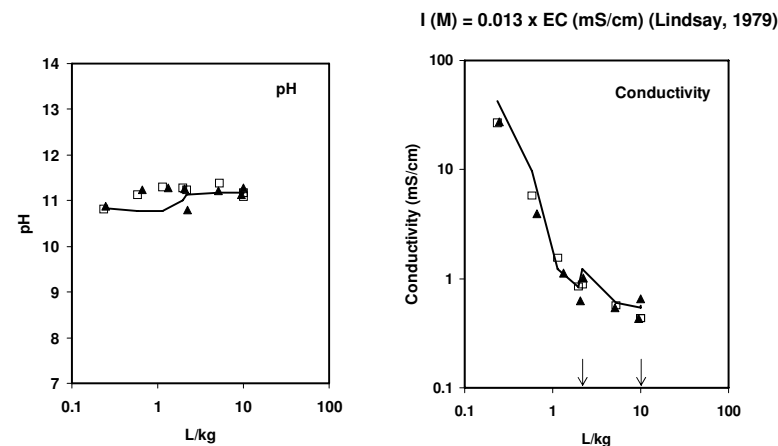
- Advective/dispersive transport of water
- Flow interruptions of 77 h at $L/S \approx 2$ and 70 h at $L/S \approx 10$
- Response of conservative element (e.g. Cl) to flow interruptions indicative for physical non-equilibrium processes $\rightarrow$ diffusional mass transfer from stagnant pores/zones
- 'Dual porosity' approach



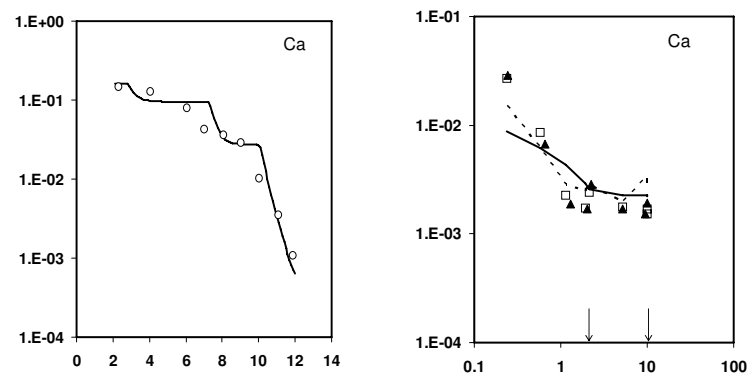
Major element dissolution/precipitation and ANC



Reactive transport model: pH and conductivity



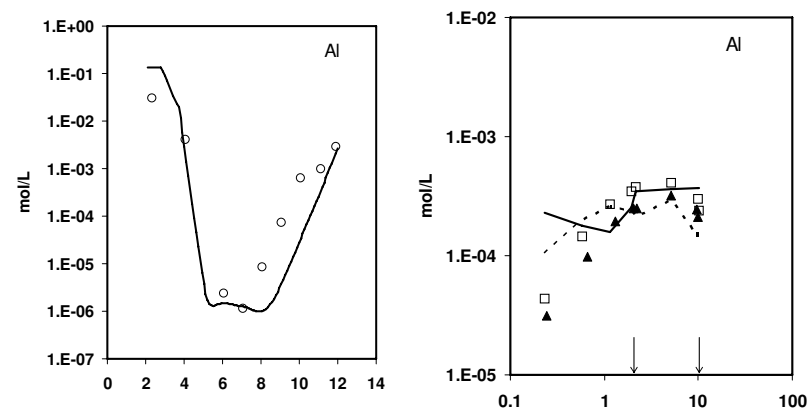
Ca: pH-dependence and percolation test



Dijkstra et al., 2006 (submitted for publication)

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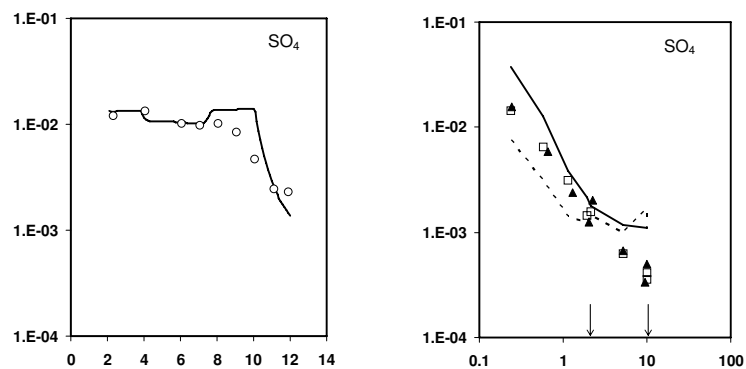
Al: pH-dependence and percolation test



Dijkstra et al., 2006 (submitted for publication)

www.ecn.nl

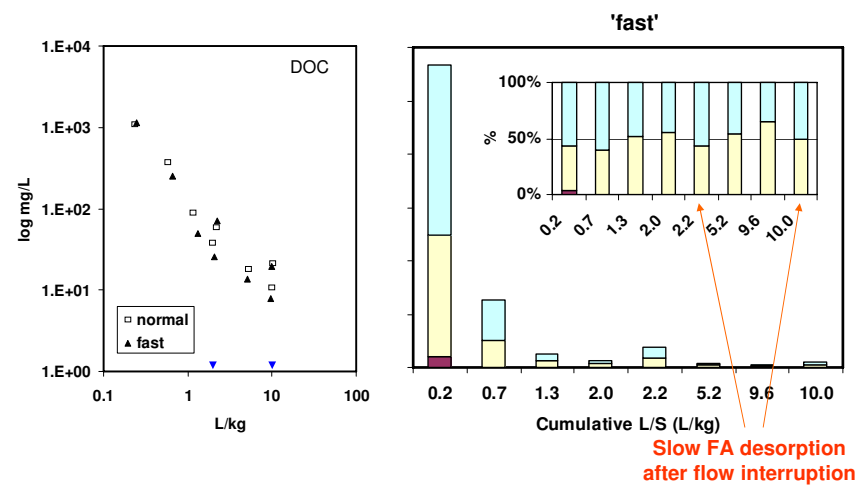
SO₄: pH-dependence and percolation test



Dijkstra et al., 2006 (submitted for publication)

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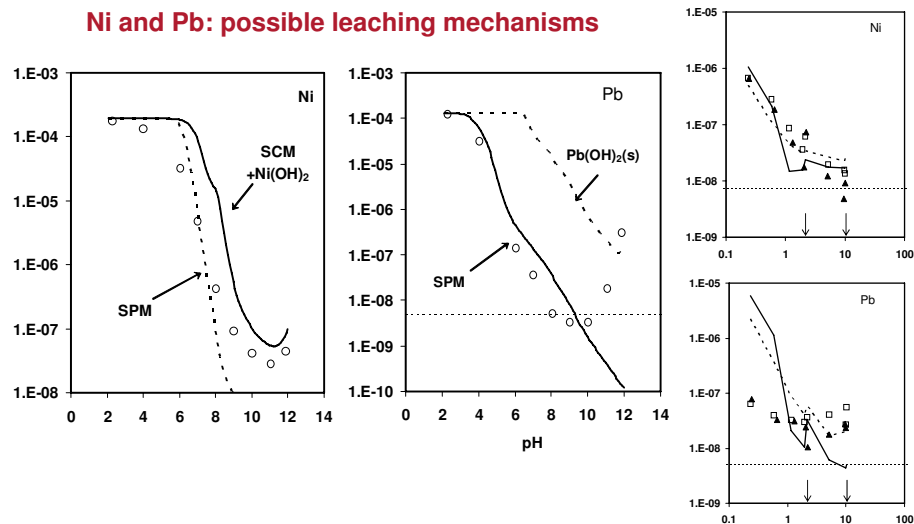
Characterisation of DOC in percolation test leachates



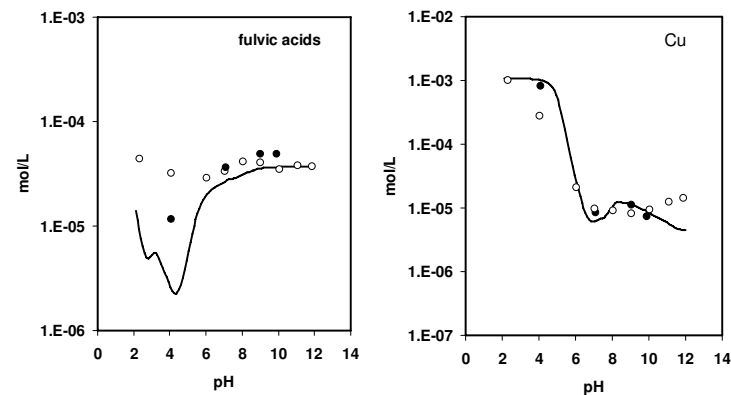
Van Zomeren, A., Comans, R.N.J., 2006 (submitted for publication)
Dijkstra J.J. et al., 2006 (submitted for publication)

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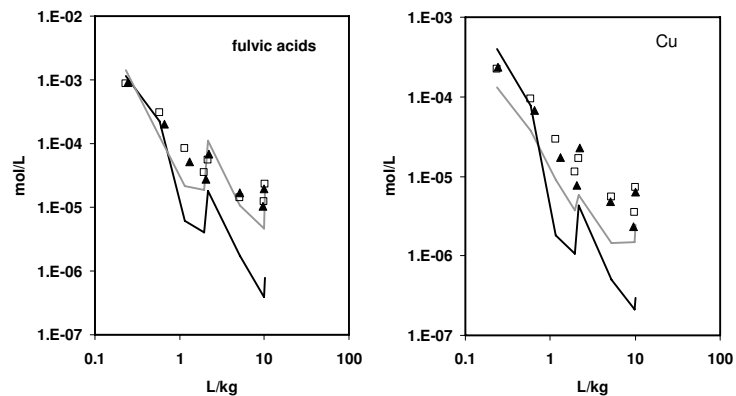
Ni and Pb: possible leaching mechanisms



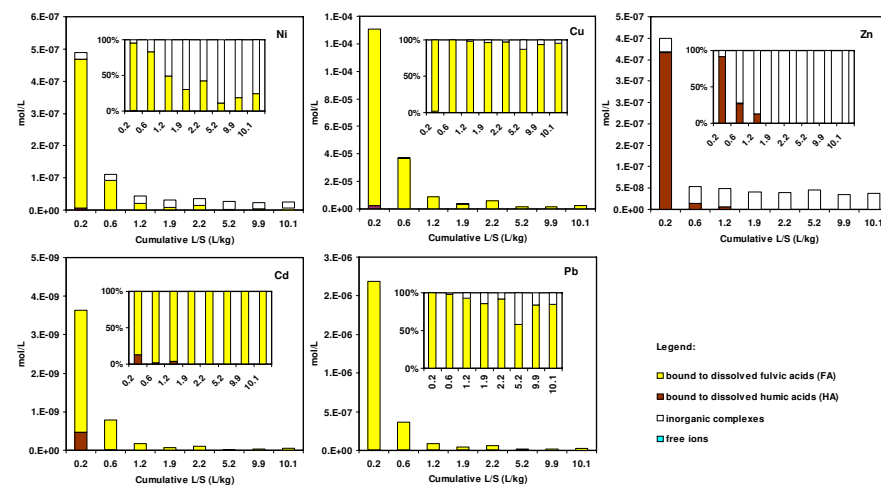
Fulvic acids and Cu: pH-dependence



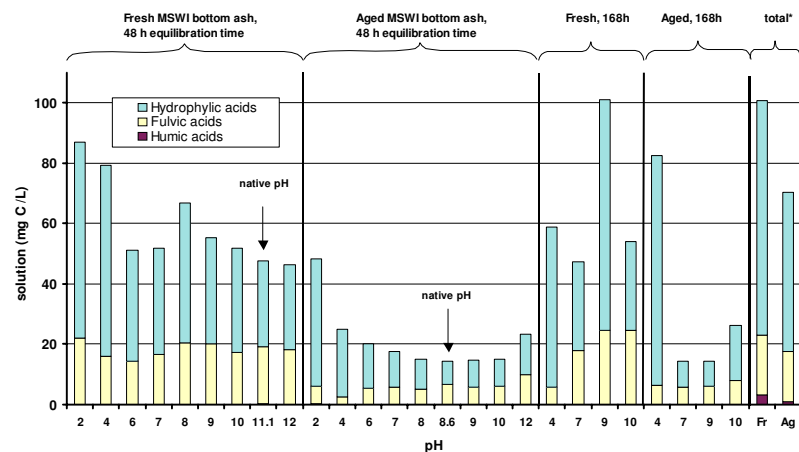
Fulvic acids and Cu: percolation test



Metal speciation in solution



Practical application: Quality improvement MSWI- bottom ash by 'accelerated aging': characterization of DOC

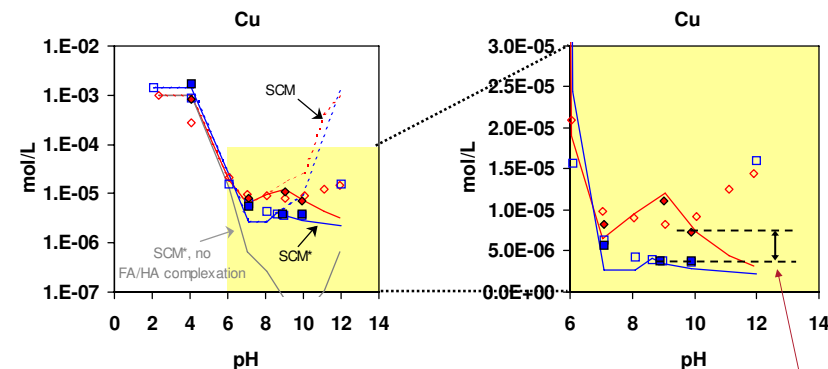


Dijkstra J.J. et al., *Environmental Science and Technology* 40, 4481-4487 (2006).

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Bottom ash treatment by accelerated ageing: effect on Cu

900 tons MSWI-BA in a composting facility, at elevated pCO_2 and relative humidity



Factor 2-3 reduction in Cu leaching quantitatively explained by retention of FA in bottom ash matrix after ageing

Dijkstra J.J. et al., *Environmental Science and Technology* 40, 4481-4487 (2006).

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Conclusions

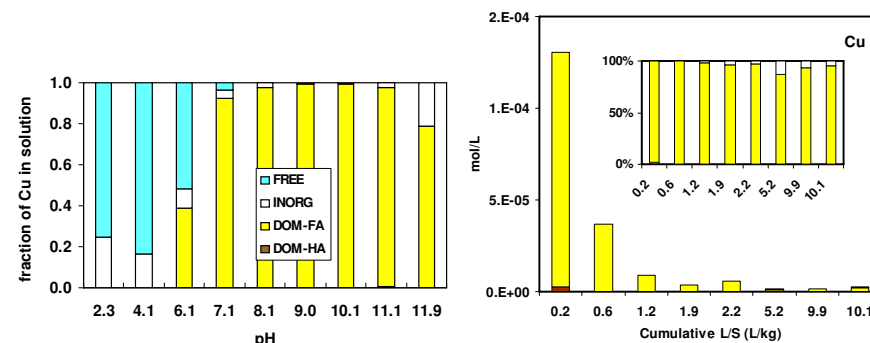
- "Multi-surface" geochemical (reactive transport) modelling enables strongly improved model prediction and understanding of contaminant source terms
- Novel aspects:
 - characterisation of DOC in terms of its reactive components (HA and FA)
 - incorporation of mechanistic models for the binding of metals to HA and FA
 - incorporation of a surface complexation model that predicts FA concentrations
 - a model that captures effects of non-equilibrium processes
- Same geochemical model adequately describes observed leaching patterns as a function of both pH and L/S for broad range of major and trace elements
- Very promising application of equilibrium-based geochemical models to dynamic leaching of heterogeneous contaminated materials

Future challenges:

- more mechanistic description of FA/HA solid/liquid partitioning
- more accurate description of acid/base buffering
- kinetic and redox processes

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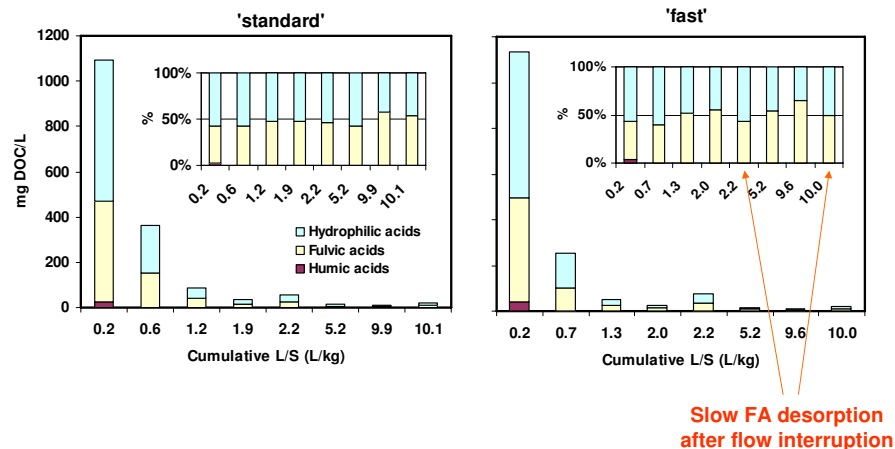
Cu speciation: pH-dependence and percolation test



Dijkstra et al., 2006 (submitted for publication)

www.ecn.nl

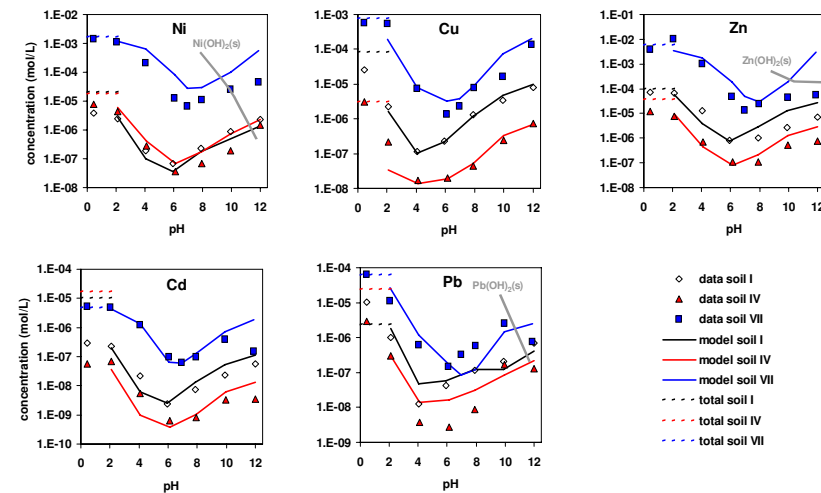
DOC characterisation in leachates from "standard" and "fast" column



* Van Zomeren, A., Comans, R.N.J., 2006 (submitted for publication)
** Dijkstra J.J. et al., 2006 (submitted for publication)

www.ecn.nl

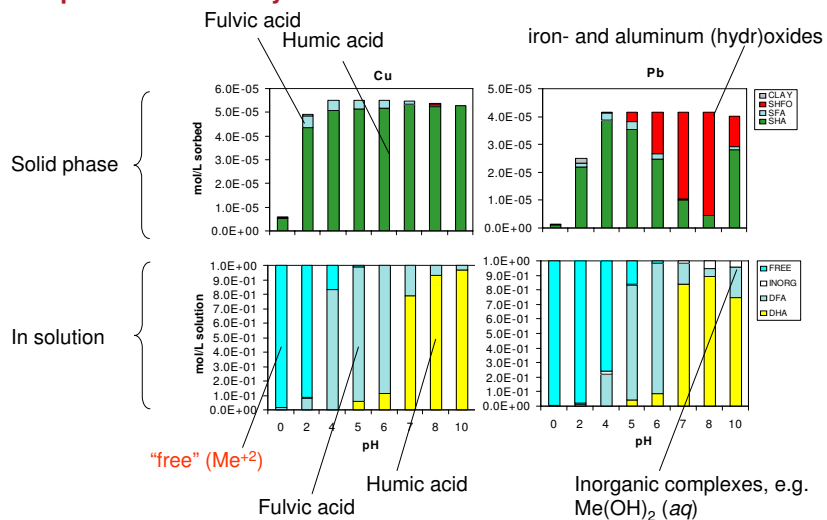
Leaching of heavy metals from contaminated soils



Dijkstra et al., *Environmental Science and Technology* (2004), 38, 4390-4395

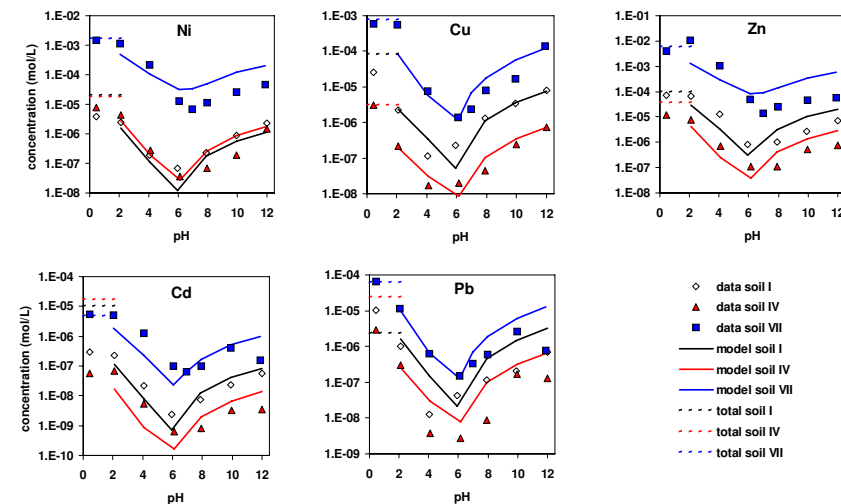
www.ecn.nl

Speciation of heavy metals in contaminated soils



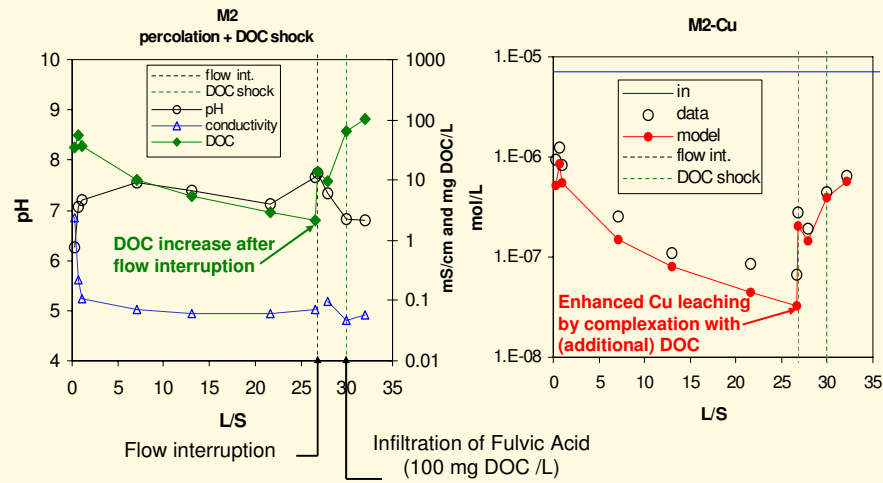
www.ecn.nl

"Minimum scenario"



www.ecn.nl

Effect of DOC on Cu mobility: enhanced Cu leaching by DOC increase



pH dependence test interpretation throughout mineral dissolution/precipitation processes

Ligia BARNA

INSA Lyon, LAEPSI, 20 av. A.Einstein, 69621 Villeurbanne, France

since 2005 at INSA Toulouse, LIPE, 135 av. de Rangueil, 31077 Toulouse, France

TOPIC

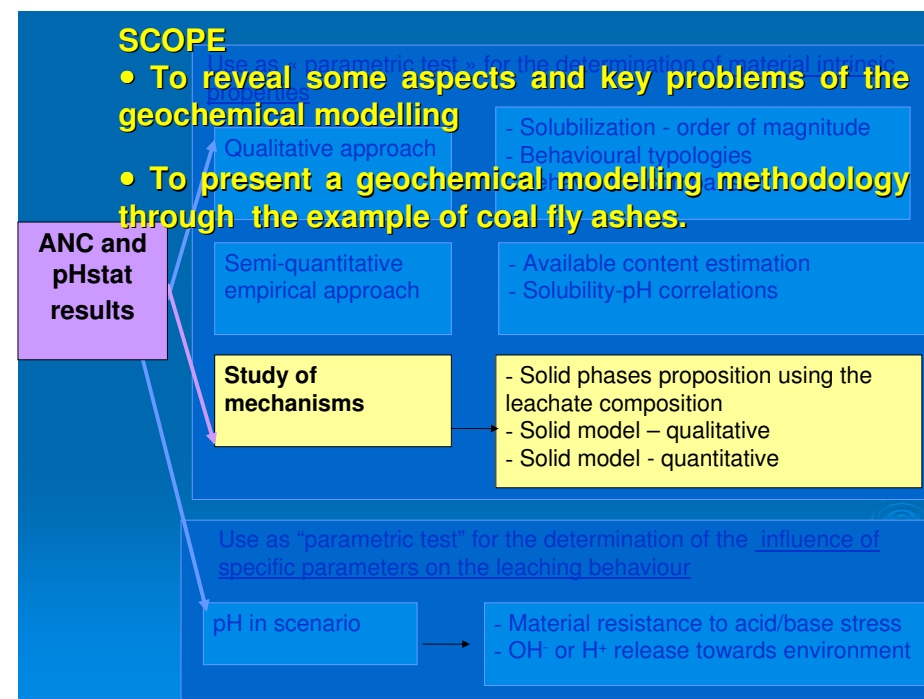
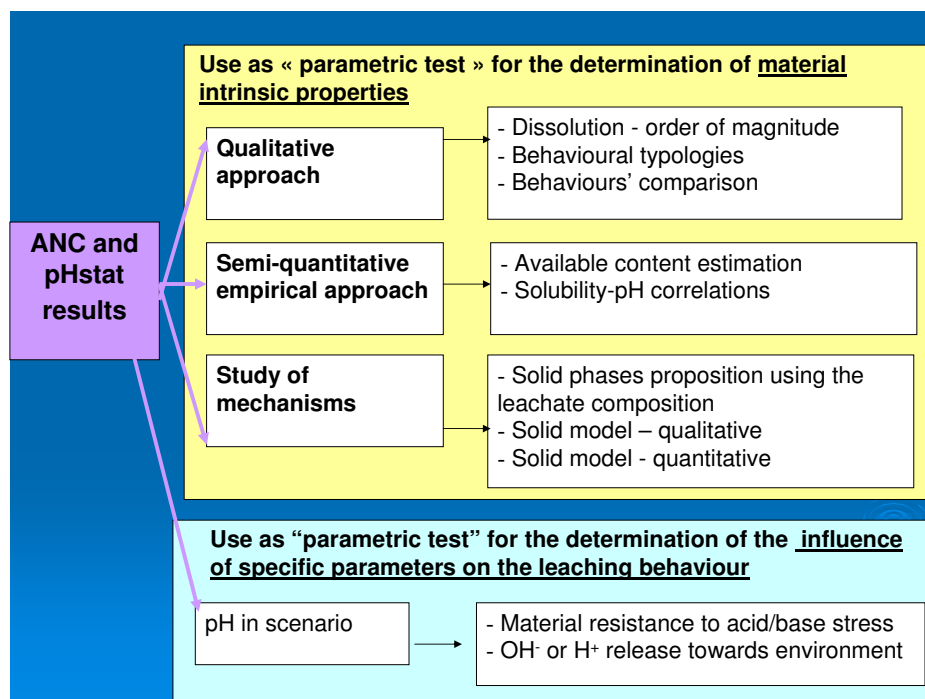
⇒ The EU standards **pHstat** and **ANC test** are more and more used for geochemical modelling proposes.

Concerning the test results use, the literature survey revealed :

- a broad variety of interpretation approaches,
- a current tendency towards the quantitative modelling approaches
no reference or modelling guide are available at present

Some aspects of the test use for geochemical modelling :

- modelling objectives - often not defined
- the equilibrium state of the solid/liquid system - not investigated
- the time scale of the experiments - extrapolations for long term
- validation possible approaches - no validation



Study of mechanisms

- Solid phases proposition using the leachate composition
- Solid model – qualitative
- Solid model - quantitative

Some aspects and key problems of the geochemical modelling using the leaching test data

Tools

Well-known geochemical modelling tools : PHREEQ, MINTEQ, Geochemical Workbench, ORCHESTRA, ...

- solid/ liquid/ gas **equilibrium** calculations
- a strong **implication of the user** in the selection of simulation parameters

Experimental data : are they at equilibrium ?

- solid /liquid reaction **kinetics is the key parameter**, implying :
 - ⇒ the identification of a **pseudo-equilibrium state**
 - ⇒ the establishing of an appropriate **experimental time scale**

Some basic modelling principles in a solid/liquid system

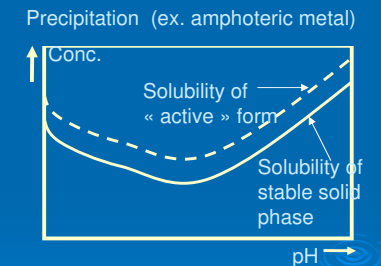
Precipitation kinetics and stability of solid phases

1) **The precipitation probability depends on T.**
 - the case of high temperature solids which can not precipitate at normal T even if $\Delta G < 0$ for the precipitation reaction.

2) **The precipitation priority rule of Ostwald :**
 the precipitate with highest solubility will form first in a consecutive precipitation reactions because kinetically favoured (the amorphous form precipitates before the crystalline form).

The phase rule

For a water/solid system (T, P cst), the maximum number of solid phases equals the number of chemical elements except H and O.



The dissolution kinetics- controlled by:

1) The mass transfer

- in fluid phase – rapid processes,
- in solid phase – slow process

2) **The surface chemistry** - slow process, depends on the liquid composition.

A modelling approach using ANC-test experimental data

Geochemical modelling objectives :

- 1) Identification of the chemical footprint of the system waste/water
- 2) Identification of main processes responsible for minor elements release
- 3) Foreseeing of the leaching behaviour at short and mean term

Requirements for achieving the objectives :

To have the capability for performing a mass balance at every time

partial knowledge of the solid and characterisation of the liquid

Relevant hypotheses on the process thermodynamics and kinetics

Relevant, complementary experimental program

liquide
solide
close

liquide
solide
open

complete knowledge of the solid material (chemistry, thermo., kinetics)
 an ideal case

Avoid arbitrary experimental conditions ! (L/S, time,...)

A modelling approach using ANC-test experimental data

Main steps

Case : partial knowledge of the solid and characterisation of the liquid

- **Elementary total content** - necessary in order to:
 - perform mass balance calculations
 - estimate the available content for soluble elements.
- **Determination of the pseudo-equilibrium state** in laboratory conditions
 -evaluation by a kinetic study

Remark the common test conditions are :

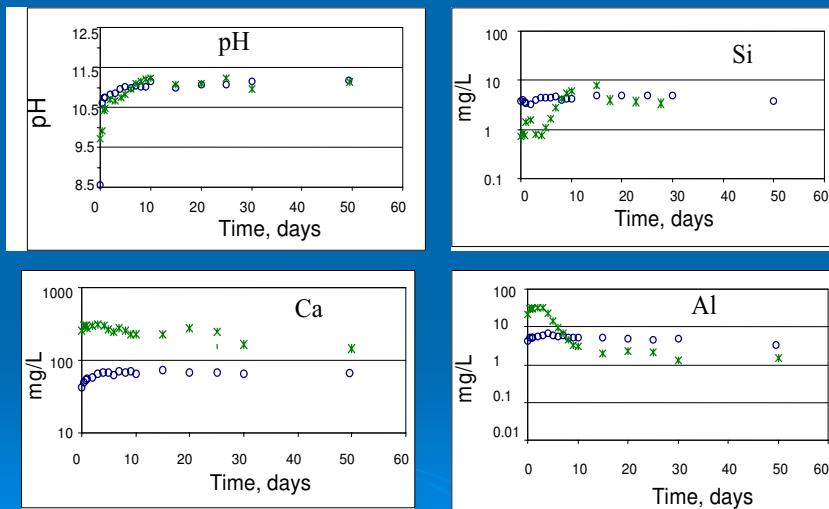
- a first contact of the material with water
- a closed isolated system and
- a short time scale

Mineralogical composition

- XRD for major phases identification
- More sophisticated investigation methods for minor phases ?
- Literature data

Example : Dissolution kinetics of a fly ash

Pseudo-steady state : after 10 days
This result doesn't exclude the possibility of ongoing slow dissolution reactions beyond 10 days.



Legend : ○ L/S=10 mL/g, ✕ L/S=1 mL/g

A modelling approach using ANC-test experimental data

Use of ANC test data Main steps

- 1) *Use of the leachate composition for a preliminary calculation*
Saturation index SI - valid parameter only for **rapid, equilibrium** solid-liquid reactions
- 2) *Building of a rough solid model* using all information on its mineralogy (knowledge, literature) + leachate composition and C curve shape
⇒ Proposition of initial phases :
 - Soluble phases or total dissolved phases - Corroboration with the leachate concentrations (Na, K, Cl, sulphates, chromates, ...)
 - Carbonates
 - iron oxides, hydroxides + surface complexes (from curve shape)
 - Silicates - corroboration with the material buffer capacity
- 3) *Neoformations - hypothesis*
 - temperature dependent precipitations *kinetics
 - pH dependent precipitations *precipitation priority rule
 - surface complexations

Example : Geochemical model for a fresh fly ash

Solid phases considered in the rough model

Solid phases :

- BaCrO₄
- BaHAsO₄·H₂O
- Periclase (MgO) or Brucite (Mg(OH)₂)
- Calcite (CaCO₃)
- CaMoO₄
- Ferrihydrite (Fe(OH)₃)
- Gibbsite (Al(OH)₃(c))
- Gypsum (CaSO₄·2H₂O)
- Halite (NaCl)
- Okenite (CaSi₂O₄(OH)₂·H₂O)
- Portlandite (Ca(OH)₂)
- Solid solution (BaSr)(CrS)O₄
- Sylvite (KCl)
- Al(OH)₃(a)
- SiO₂(a)

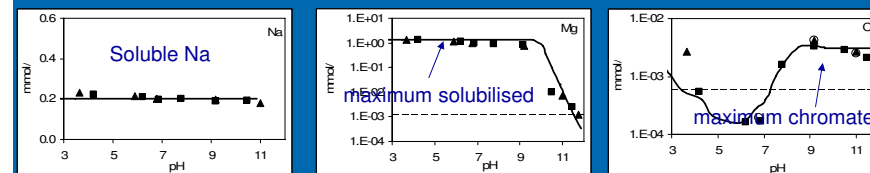
- from SI
- from mine. + leachate hypothesis

A modelling approach using ANC-test experimental data

Main steps

4) Quantitative modelling - Fitting the **reactive** phases' quantities

- on the C – pH curve

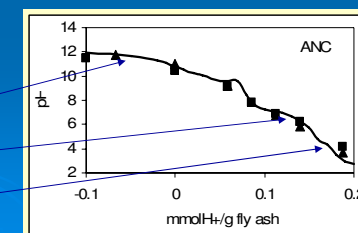


- on the ANC curve

Ca containing silicates

carbonates

Gibbsite



A modelling approach using ANC-test experimental data

Main steps

Validation and improvement

Additional experimental data are needed !

- a dynamic open-system test, or
- an equilibrium (closed-system) test applied on leached (modified) solid

Model improvement

- an iterative approach **simulation-validation** involving different experimental data

Example : Geochemical model for a fly ash

* Use of percolation column data

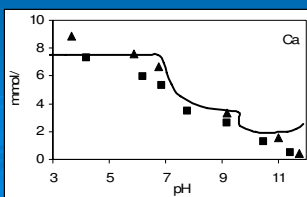
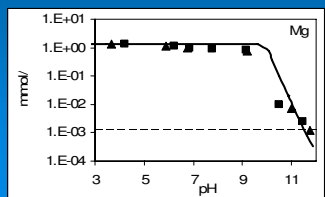
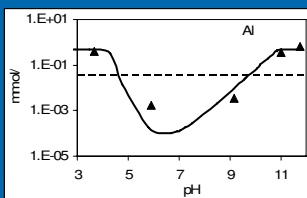
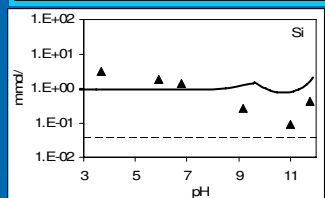
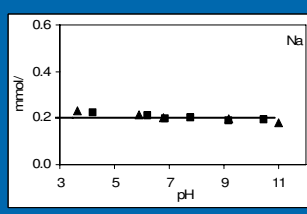
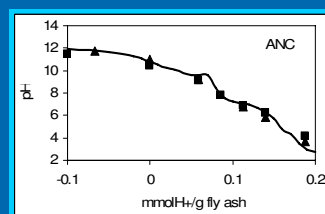
- introduction of a solid solution and kinetic reactants

Example : Geochemical model for a fly ash

Solid phases and fraction of elemental content considered in the model

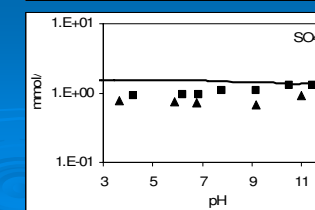
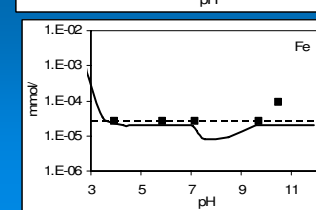
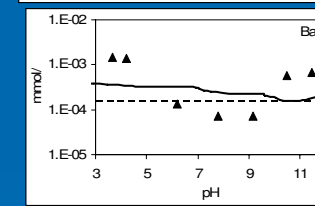
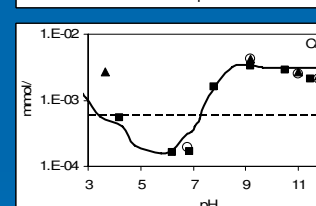
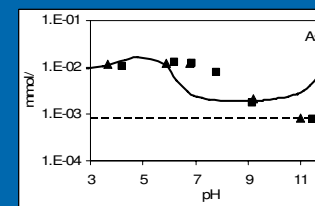
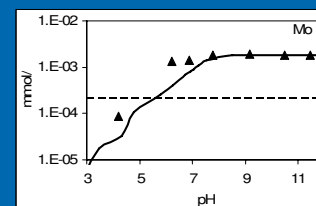
Solid phases :	mmol/kg fly ash	Element	% of TC
BaCrO4	0.05	Al	0.6
BaHAsO4.H2O	0.7	As	104.9
Periclase (MgO) or Brucite (Mg(OH) ₂)	13	Ba	80.7
Calcite (CaCO ₃)	40	Ca	65.5
CaMoO ₄	0.018	Cr	1.4
Ferrihydrite (Fe(OH) ₃)	0.6	Cr VI	104.0
Gibbsite (Al(OH) ₃ (c))	5	Fe	3.0
Gypsum (CaSO ₄ .2H ₂ O)	10	K	2.9
Halite (NaCl)	2	Mg	3.1
Okenite (CaSi ₂ O ₄ (OH) ₂ .H ₂ O)	20	Mo	18.8
Portlandite (Ca(OH) ₂)	9	Na	4.2
Solid solution (BaSr)(CrS)O ₄	20	S	100.0
Sylvite (KCl)	2.4	Si	6.4
Al(OH) ₃ (a)	neo-formation	Sr	100.7
SiO ₂ (a)	neo-formation		
Kinetic reactants	mmol/kg fly ash	parameter	
Albite (NaAlSi ₃ O ₈)	23.8	p ₁ =5.10 ⁴	
K-feldspar (KAlSi ₃ O ₈)	238	p ₁ =1.10 ⁶	
Ca-Olivine (Ca ₂ SiO ₄)	4.7	p ₁ k _r =2.10 ⁻⁵	

Fly ash - ANC results



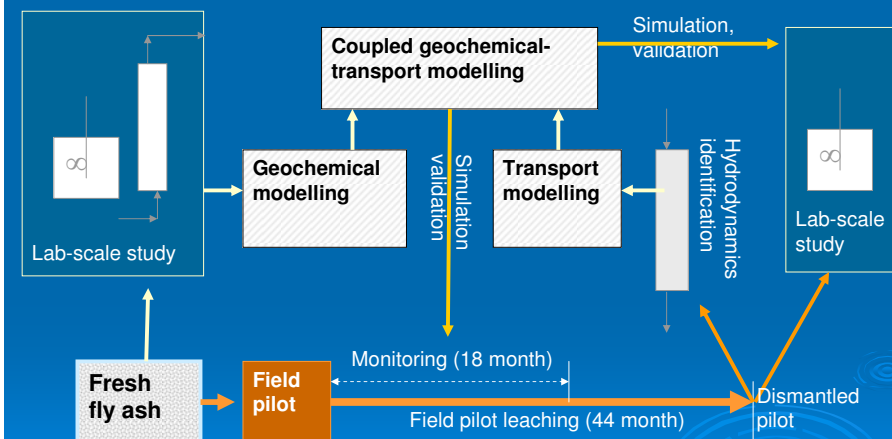
Legend :
 ■ assay 1
 ▲ assay 2
 — simulation
 - - detection limit

Fly ash - ANC results



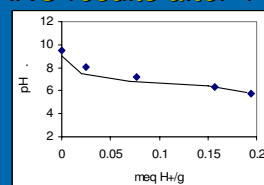
Legend :
 ■ assay 1
 ▲ assay 2
 — simulation
 - - detection limit

Example of a multi-scale « modelling – simulation – validation » approach

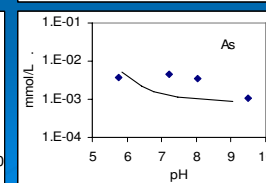
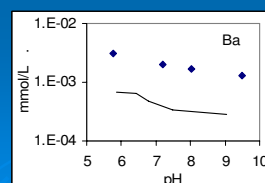
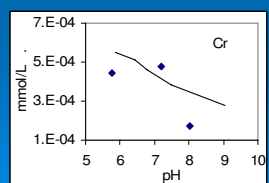
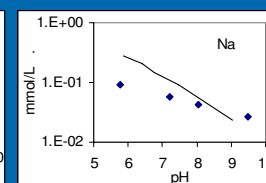
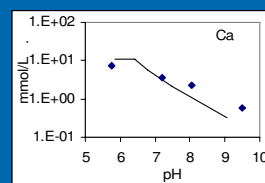
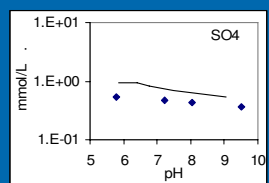


Reference : L.Tiruta-Barna, Z.Rakotoarisoa, J.Méhu, Assessment of the multi-scale leaching behaviour of compacted coal fly ash. *Journal of Hazardous Materials*, 2006, B137, 1466-1478

ANC results after 44 month of leaching under natural conditions



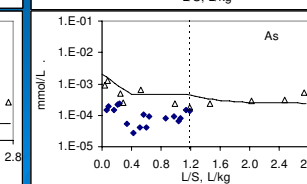
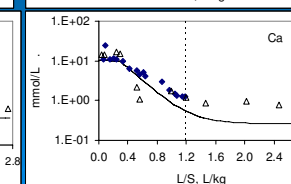
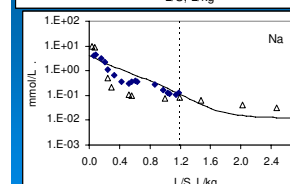
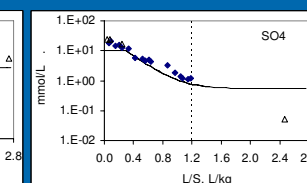
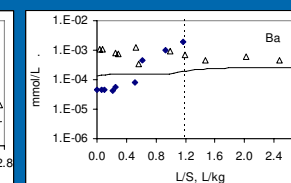
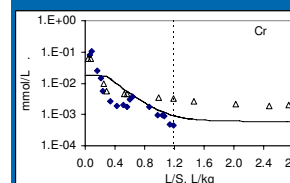
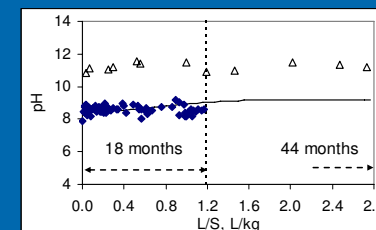
Legend :
♦ experiment
— simulation



Leaching behaviour foreseeing

Pilot leaching results 0 – 18 month

Legend :
♦ experiment
— simulation
▽ column experiment



Conclusions

Specific test contribution for the geochemical modelling

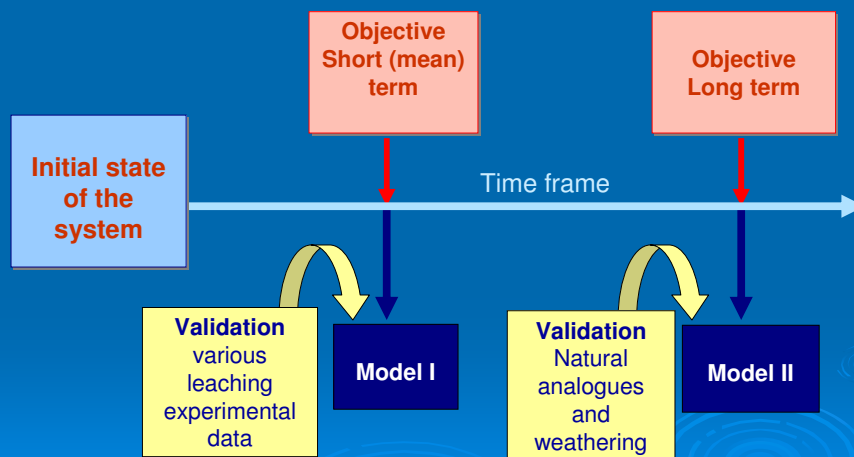
- 1) The neutralisation curve (ANC curve) - useful data for :
 - quantitative determination of acid/base buffering phases
 - chemical footprint of the material
- 2) Ensures pH conditions for the complete dissolution of some solid phases
 - quantification of these phases (elements available quantities)
- 3) Identification and quantification of minor phases containing trace elements
- 4) Identification of specific chemical mechanisms like
 - surface complexation
 - interactions with soluble organic matter
- 5) The leachate composition (C and pH)
 - serves as fitting parameters for the quantitative model

Conclusions

Specific test contribution for the geochemical modelling ...and limitations

- 6) ANC test doesn't replace the mineralogical investigation (knowledge)
- 7) Only the most soluble phases are "visible" and can be identified; the low soluble or slow solubilised phases are "hidden"
- 8) Test time scale inappropriate for long term forecasting

Appropriateness
objective – experiments - models



Long-term prediction of contaminant leachability from ashes and cementitious materials

How uncertain can geochemical and
hydrological information be?

Annette Johnson & Ann-Kathrin Leuz
Eawag
Switzerland

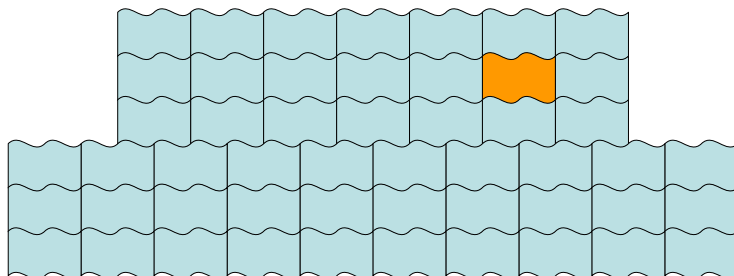
Long-term prediction of contaminant leachability from cementitious materials

How uncertain can geochemical and
hydrological information be?

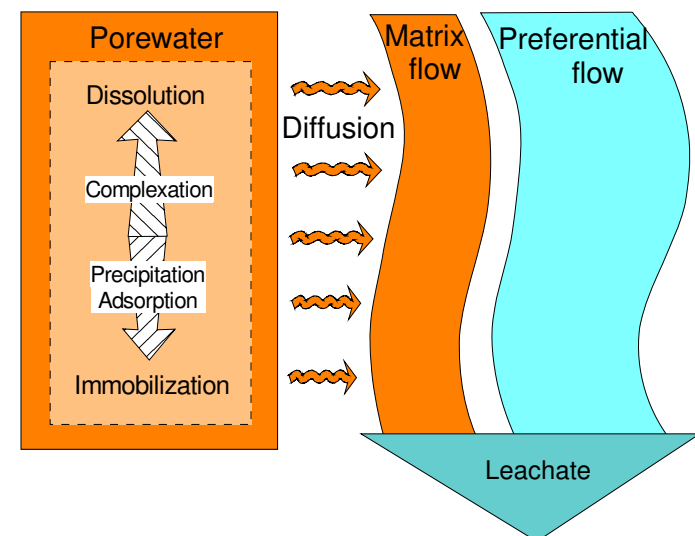
Annette Johnson & Ann-Kathrin Leuz
Eawag
Switzerland

The answer

It depends on the question



Geochemistry...diffusion...hydrology



Geochemistry

An overview of what we know and what we don't, for cementitious systems

We are more familiar with metal(loid) chemistry than the matrix, particularly regarding kinetics

Cementitious systems still pose a challenge

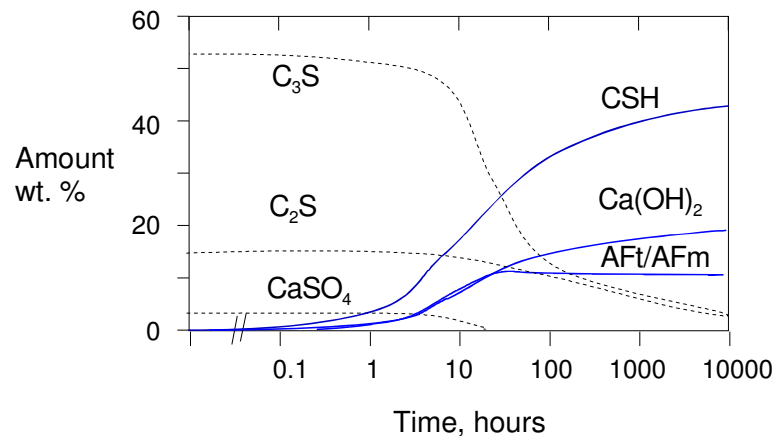
Need to know:

Binding mechanisms and solubility control with time

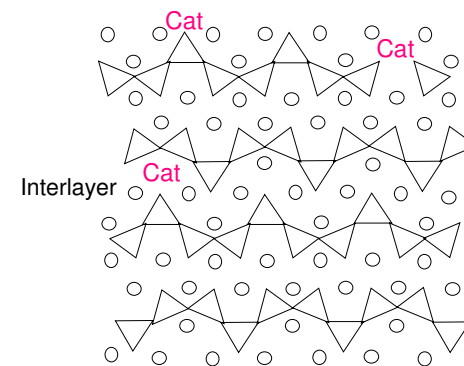
- as f(cement composition)
- as f(metal(loid) concentration)
- as f(pH) and solution composition

Hydration of OPC cement clinker

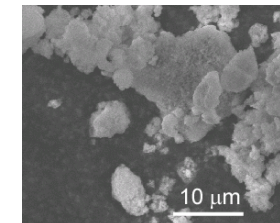
water:cement = 0.4 : 1



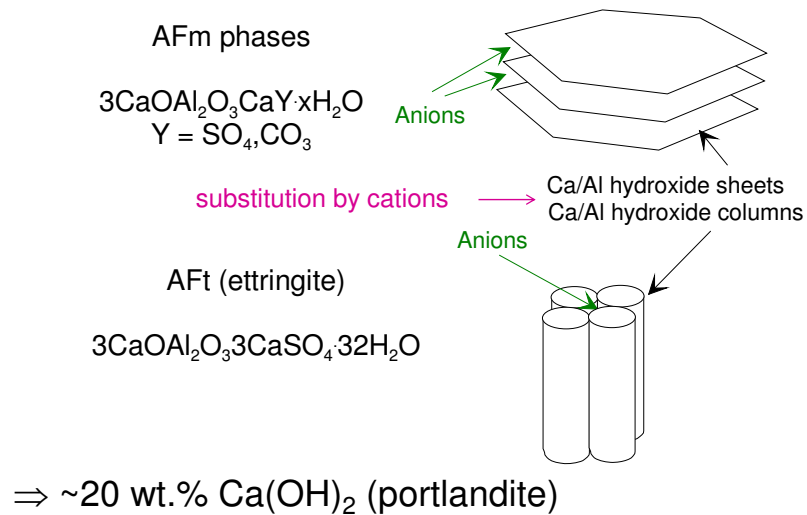
Hydration products: Ca silicate hydrate (50 wt.%)



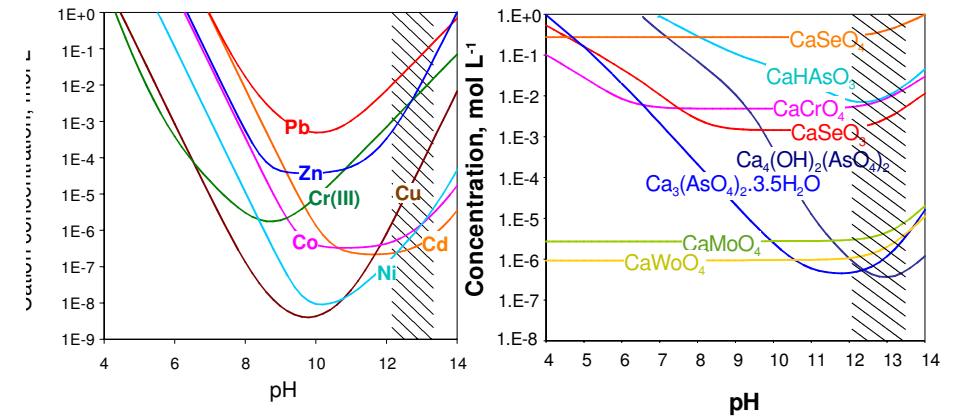
Calcium silicate hydrate



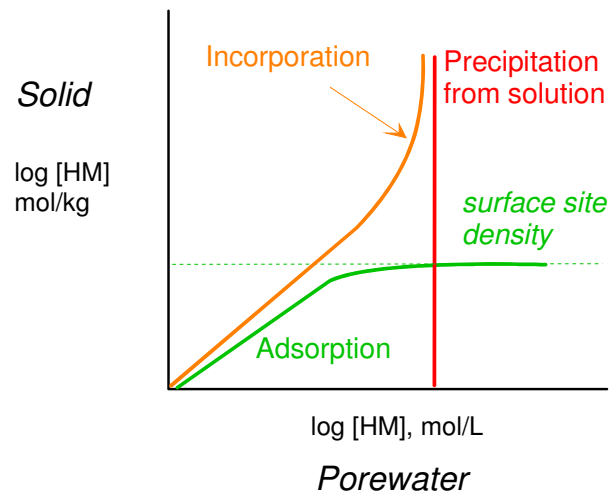
Hydration products: Basic Ca aluminates (~18 wt.%)



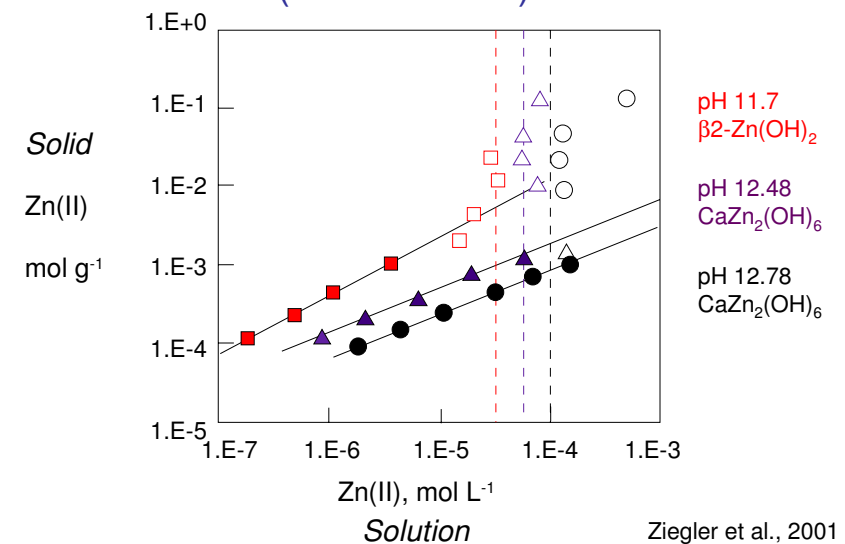
Solubility of heavy-metal cations



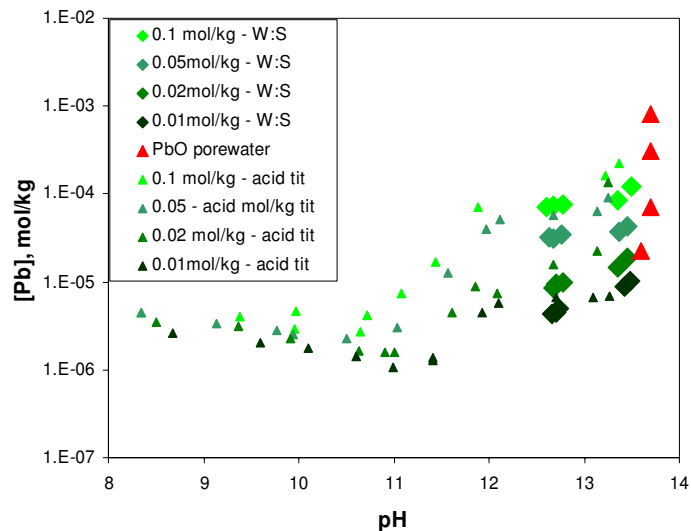
Porewater concentrations (Sorption isotherms)



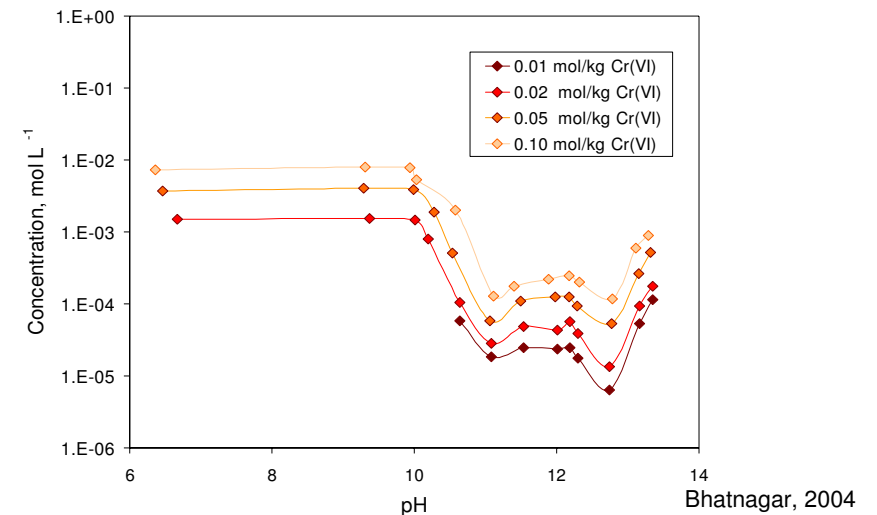
Zn(II) binding to C-S-H (Ca:Si = 1:1)



Hydrated OPC doped with PbO



Solubility of chromate in doped OPC hydrated cement pastes

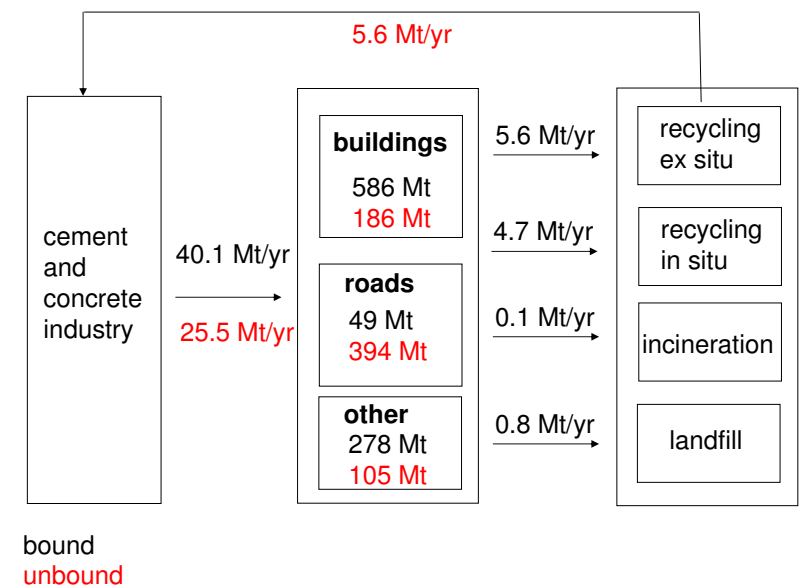


Cement & concrete industry in Switzerland

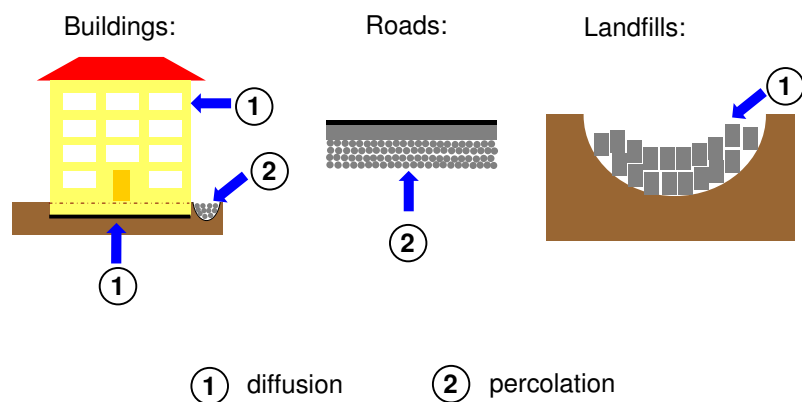
- Is there an environmental impact resulting from changes in the cement and concrete industry?
- Change in raw and secondary materials
 - Recycling of C&D wastes

➡ Zn, Pb, Cr(VI), Se, Sb

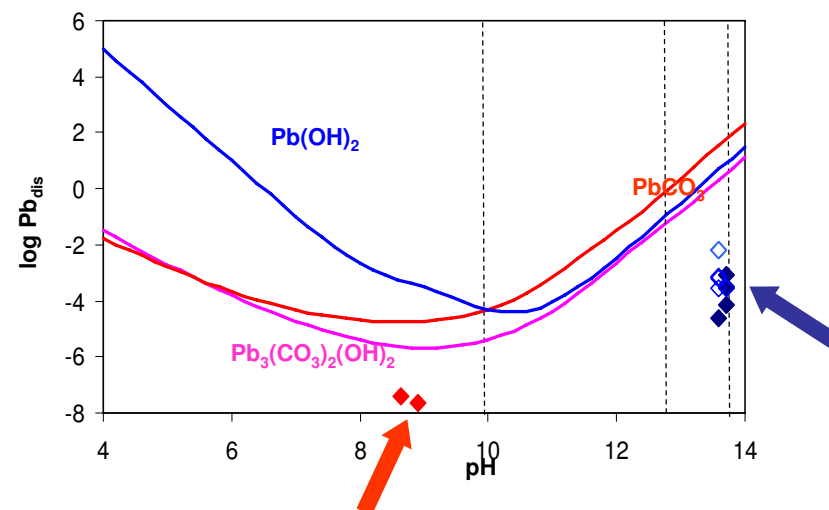
Flow analysis of concrete in CH



Leaching scenarios



Porewater concentrations: Pb solubility in hydrated OPC



Preliminary results

	$Pb_{leached}$ [mg/kg]	$Cr_{leached}$ [mg/kg]
Buildings:		
1:	$1.5 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$
2:	$1.7 \cdot 10^{-2}$	2
RC:	$3.1 \cdot 10^{-2}$	2
Roads		
2:	$3.7 \cdot 10^{-3}$	2
landfills		
1:	$5.1 \cdot 10^{-2}$	$2.5 \cdot 10^{-6}$

Total concentrations: 10 44

Comparison with rain water

	rain water [mg/(m ² Jahr)]	concrete** [mg/(m ² Jahr)]
Pb	7	5
Zn	21	127
Sb	0.2	0.06
Cr	1	490
Se	0.1	0.04

** normalized by built-up areas

Concluding remarks

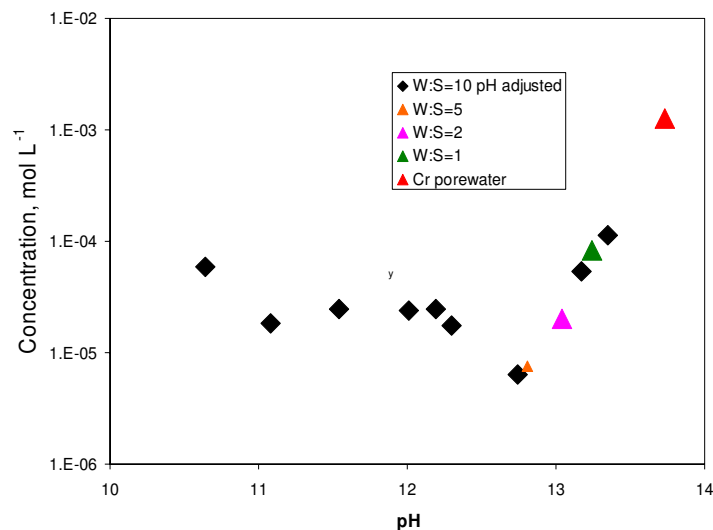
- Decisions were actually made on the basis of leach tests
- Our research needs to focus on
 - i) on determining long-term biogeochemical behaviour
 - ii) on developing realistic scenarios (particularly D_{obs} , carbonation, hydrology)

Acknowledgements

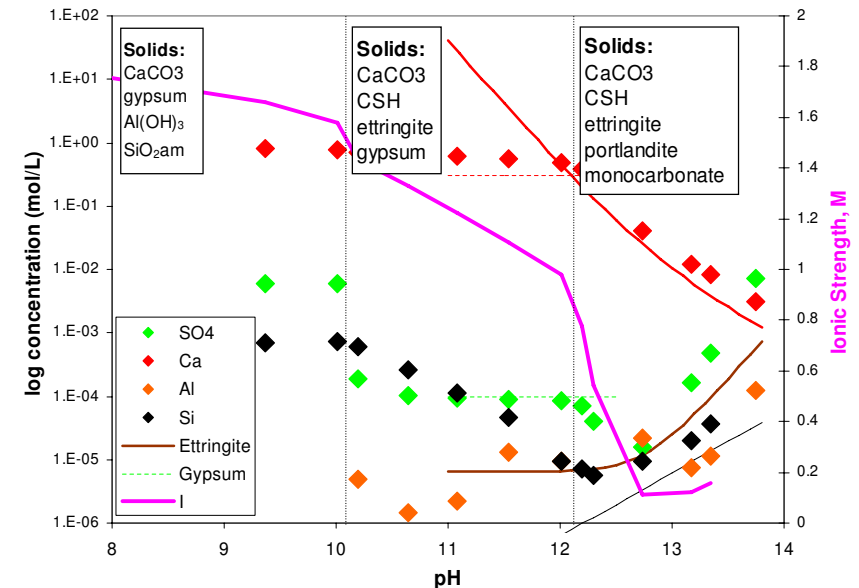
Amit Bhatnagar, Petra Braun, Hermann Moench, Barbara Lothenbach, Frank Winnefeld

Susanne Kytzia and Christina Seyler (ETH)
The Swiss National Science Foundation

pH dependence ($0.01 \text{ mol kg}^{-1} \text{ CaCrO}_4$) acid/base addition vs. change in W:S ratio



Minerals as f(acid addition)



Source-term Conceptual Models and Challenges in Predicting Long-term Performance of Cement Stabilized Waste Forms

D.S. KOSSON, F. SANCHEZ, A. GARRABRANTS*
H.A. van der SLOOT, J.C.L. MEEUSSEN**

*Vanderbilt University, Nashville, USA

**ECN, Petten, The Netherlands

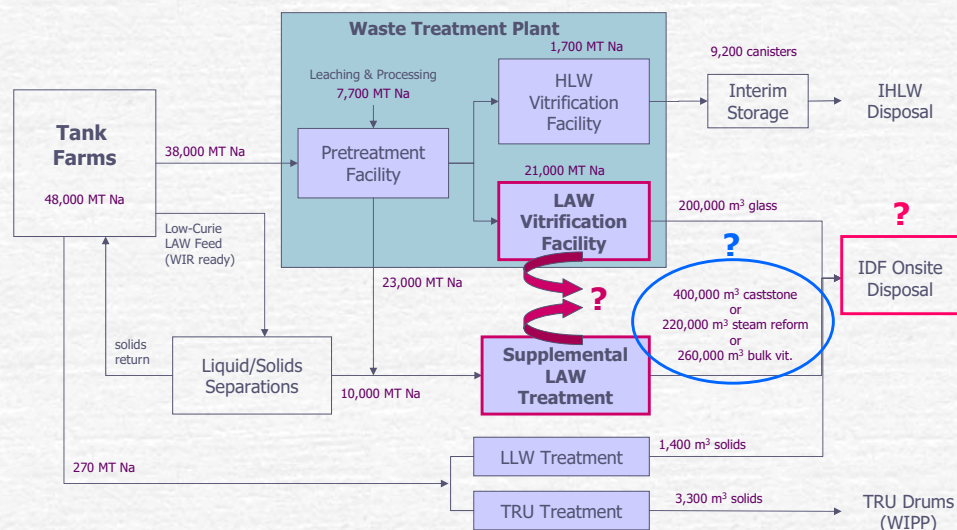
Source Term: from characterization to prediction
Paris - 19 October 2006

Hanford Tank Waste

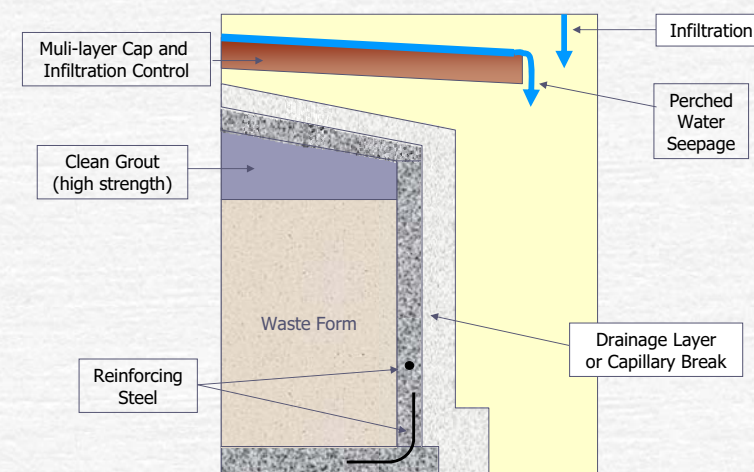
- 144 Underground Tanks
 - Concrete reinforced carbon steel
 - 10⁶ gallon capacity
 - Single and double shelled
- Tank Waste
 - Supernatant, sludge, filter cake
 - 2x10⁸ m³ of radioactive waste
- DOE Remediation by 2028



Hanford Tank Waste Remediation



Generic Vault Disposal System



Motivation

- Need for better estimates of long-term constituent release for near-surface disposal of cementitious and other non-vitrified waste forms.
- Applicability
 - HLW tank closure using grout
 - Disposal of saltstone & similar wastes at SRNL, INL, Hanford
 - Primary and secondary waste streams from steam reforming
 - Secondary waste streams from vitrification
 - Waste Treatment Acceptance Criteria
 - Operational Controls
 - Management of future wastes from reprocessing/recycling (GNEP)
- Primary Constituents of Concern
 - Long lived & Mobile: Tc-99, Np-237, Se-79, I-129, C-14, U
 - Mobile: Cs-137, Sr-90, Nitrate, tritium

Questions

What basis should be used to:

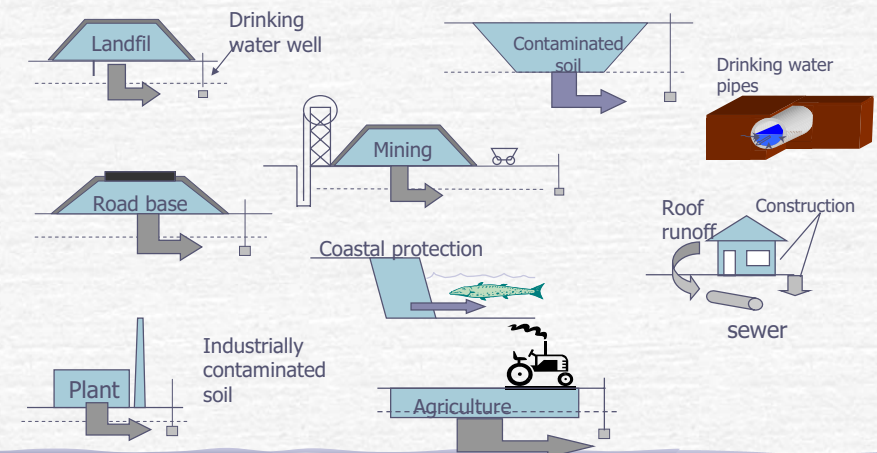
- Define the appropriate type of waste form, disposal system and location for specific wastes?
- Estimate long-term waste form and disposal system performance?
- Establish treatment (operational) criteria?
- Define monitoring requirements (pre-cursors) that enable pre-emptive action to avoid system failure?

Constituent Release by Leaching

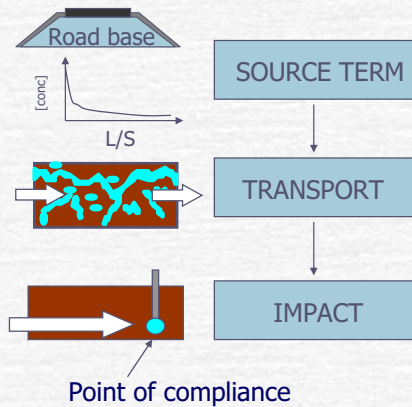
- Primary Factors
 - System Integrity
 - Engineered and Institutional System
 - Waste Form Performance
 - Physical Integrity
 - Water Contact
 - Moisture Status
 - Oxidation Rates and Extent
 - Constituent Chemistry and Mass Transport

DIFFERENT IMPACT SCENARIOS.....

16 Dec. 2003
DG ENV



..... SIMILAR PROBLEM

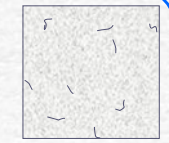


Different for each scenario - material, changes over time (carbonation, redox), etc.

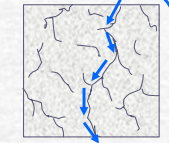
Transport in unsaturated zone and saturated zone to point of compliance - Similar for each scenario

Processes and Impacts

Physical Integrity & Water Contact



- Monolithic Matrix**
 - Flow-around
 - Low interfacial area
 - Diffusive release



- Stressed Matrix**
 - Flow-around/through
 - Higher interfacial area
 - Diffusion-convection



- Spalled Matrix**
 - High permeability
 - Very high interfacial area
 - Equilibrium-based release

Impact

- Need to account for the sequence of physical states and rate of changes
- Influences chemical reactions and constituent release
- Both "intact" & "degraded" cases are simplistic and may not be realistic

Conceptual Model

- Micro-cracks develop, increasing solid-liquid surface area
- Bridging of micro-cracks create macro-cracks
- Through-cracks develop over time, leading to convective flow
- Ultimate end state may be permeable matrix – release based on local equilibrium

Processes and Impacts

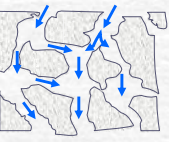
Physical Integrity & Water Contact



- Monolithic Matrix**
 - Flow-around
 - Low interfacial area
 - Diffusive release



- Stressed Matrix**
 - Flow-around/through
 - Higher interfacial area
 - Diffusion-convection



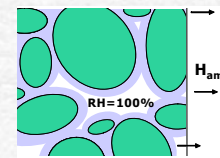
- Spalled Matrix**
 - High permeability
 - Very high interfacial area
 - Equilibrium-based release

Needed Information

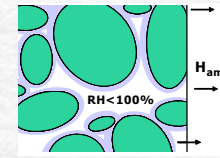
- External stresses
 - External loads
 - Differential settlement
- Material strength (e.g., Young's Modulus)
- Material pore structure
- Internal stresses
 - Shrinkage/dehydration
 - Expansive reactions within pores

Processes and Impacts

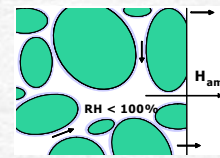
Moisture Transport



- Full Saturation**
 - Continuous Liquid
 - Discontinuous Gas



- Capillary Saturation**
 - Continuous Liquid
 - Continuous Gas

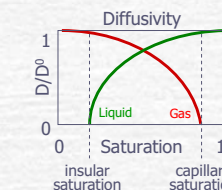


- Transition Zone**
 - Discontinuous Liquid
 - Continuous Gas



- Insular Saturation**
 - Discontinuous Liquid
 - Continuous Gas

- Completely Dry**



Conceptual Model

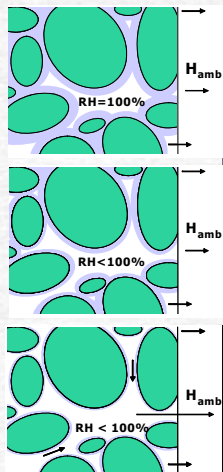
- Waste form consumes water via hydration reactions
- Moisture exchange w/environment
 - Evaporation/condensation
 - Capillary suction
 - Intermittent wetting (precipitation)
 - Percolation (degraded matrix)
- Water content determines
 - Gaseous degradation processes (oxidation, carbonation)
 - Constituent diffusion pathways

Impact

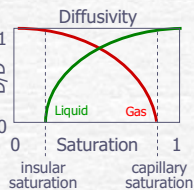
- Spatial & temporal moisture gradients
- Diffusivities are not constant over moisture regime
- Fractional saturation
 - Increases the importance of gas phase transport & reactions
 - Decreases rate of liquid phase transport

Processes and Impacts

Moisture Transport



- Full Saturation**
 - Continuous Liquid
 - Discontinuous Gas
- Transition Zone**
 - Continuous Liquid
 - Continuous Gas
- Insular Saturation**
 - Discontinuous Liquid
 - Continuous Gas
- Completely Dry**

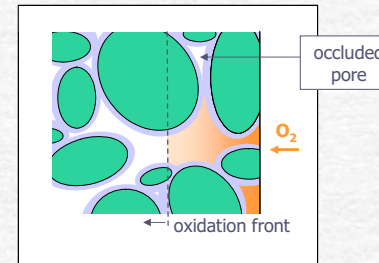


Needed Information

- Water producing & water consuming reactions
- Water retention curves (capillarity)
- Relative humidity-material saturation equilibrium
- Drying rates
- Permeability (water)
- Boundary conditions
- Episodic infiltration
- Relative humidity

Processes and Impacts

Oxidation Rates and Extent



Conceptual Model

- Waste form pores – two phase system of gas and liquid; depends on moisture content (saturation)
- O₂ transport via gaseous diffusion may be important depending on saturation.
- Oxidation may lead to change in leaching behavior
 - Increased Tc-99 release; other redox sensitive constituents

Impact

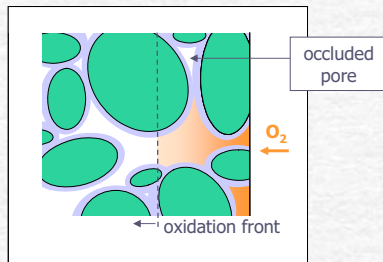
- Gas phase transport must be considered
- Flux of O₂ (gas) ~10⁵ > liquid phase flux

	Air	Water	Ratio (A/W)
D _{O2} [cm ² /s]	0.21	0.000019	1.1E+04
Conc of O ₂ [mole/L]	8.9E-03	2.6E-04	1.4E+01

(1) Wilke and Chang, 1955
(2) www.swbc.org/education/ env-engr/gastransfer/gastransf.html

Processes and Impacts

Oxidation Rates and Extent

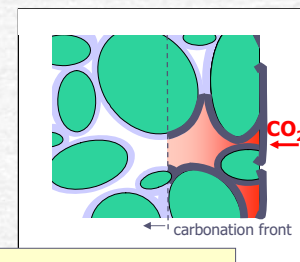


Needed Information

- Reducing capacity & redox titration
- Moisture status
- Gas phase diffusivity f(saturation)
- Liquid phase diffusivity f(saturation)
- Boundary conditions

Processes and Impacts

Carbonation

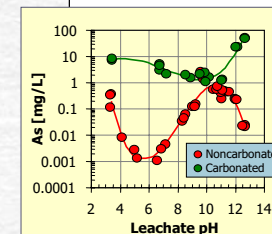


Conceptual Model

- CO₃²⁻ + Ca²⁺ → CaCO₃ (s)
 - Gas phase diffusion of CO₂
 - Liquid phase diffusion of HCO₃⁻
- Pore water pH decreased
 - Alters solubility of constituents (increase or decrease depending on species).
- Carbonation
 - Expansive precipitate – internal stress (cracking)
 - Pore blocking – increases diffusional resistance (decreases oxidation, release rates).
 - Extent and pore effects depend on waste form alkalinity and saturation

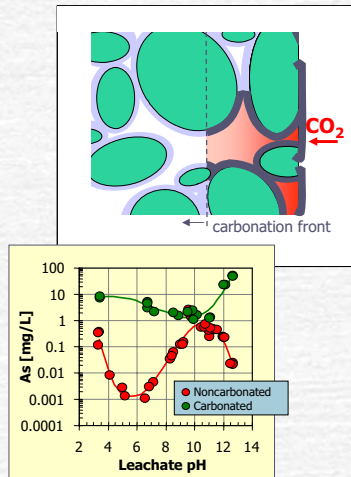
Impact

- Potential for speciation changes (e.g., As)
- Impact on sorption sites
- Pore structure changes
- May have either positive (e.g., pore capping) or detrimental (i.e., increased solubility) impacts



Processes and Impacts

Carbonation

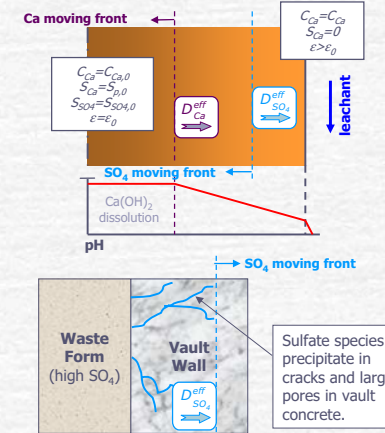


Needed Information

- Acid neutralization capacity & pH titration
- Moisture status
- Gas and liquid phase diffusivities
- Pore structure
- Boundary conditions
 - Vapor phase CO_2
 - Aqueous carbonate/bicarbonate

Processes and Impacts

Leaching of Major Constituents



Conceptual Model

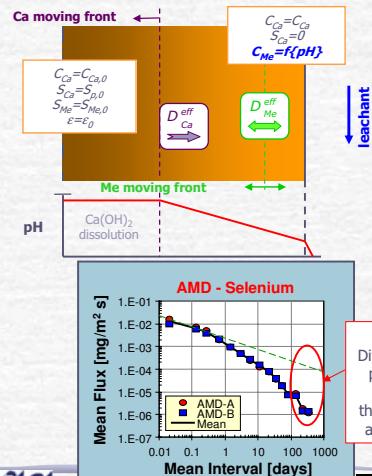
- Transport described by moving dissolution fronts
- Precipitation/reaction processes near external boundaries may significantly impact release (+ or -)
- Dissolution/diffusion of $\text{Ca}(\text{OH})_2$ and CSH control pore water pH
 - pH gradients alter trace species release
- SO_4 leaching from waste into vault attacking concrete physical structure.
- Source of SO_4 may be waste or external environment

Impact

- Mass transport estimates may not reflect the dynamic chemistry and mineralogy of the waste form.
- Release rates and extents mechanistically different from simplified assumptions, effecting predictability.

Processes and Impacts

Leaching of Trace Constituents



Conceptual Model

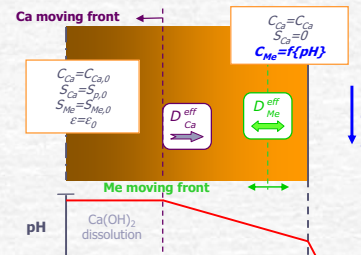
- Release based on coupled chemistry and mass transport.
- Release dependent on:
 - Moisture conditions
 - pH gradients
 - Redox chemistry
 - Boundary layer formation

Impact

- Performance assessments may over- or under-predict release

Processes and Impacts

Leaching of Major & Trace Constituents



Needed Information

- pH dependent equilibrium
- Column test
 - Pore water
 - LS evolution
- Analysis of
 - pH, EC, Eh
 - Full suite of cations and anions
 - TOC, TIC, DOC, DIC
- Boundary Conditions!

Current Studies on Secondary Waste from ORP

Motivation

- Tc-99, I-129 in secondary wastes from vitrification

Objective

- Leaching assessment of reducing grout for secondary waste treatment.
- Comparison with "ANS16.1-type" testing in synthetic ground water.

Reducing Grout

- Ground Steel Slag 43 wt%
- Class F Fly Ash 42
- OPC 7
- DI Water 7

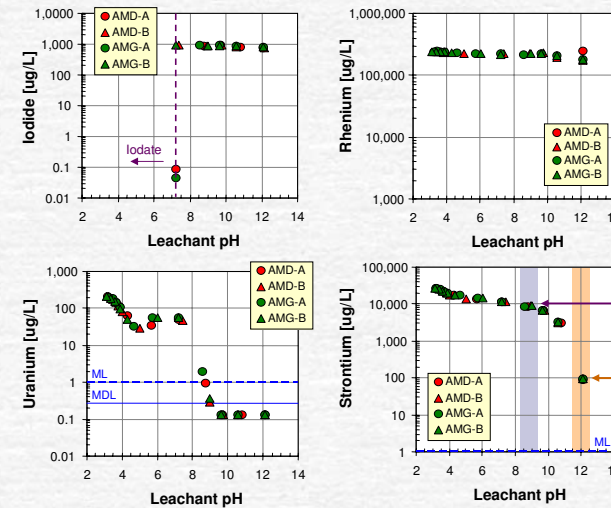
Synthetic Hanford Groundwater

- CaSO_4 1.20 mmol/L
- NaHCO_3 1.04
- $\text{Mg}(\text{HCO}_3)_2$ 0.62
- CaCl_2 0.34
- KHCO_3 0.19
- $\text{Ca}(\text{HCO}_3)_2$ 0.18

Contaminants in Reducing Grout

	mg/kg	Added As
Ag	243	AgNO_3
As(V)	1000	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$
Ba	500	$\text{Ba}(\text{NO}_3)_2$
Cd	1000	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Cu	1000	$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$
Cs	1000	CsCl
I	1214	NaI
Pb	1000	$\text{Pb}(\text{NO}_3)_2$
Re	971	KReO_4
Sb	952	Sb_2O_3
Se	751	KSeO_4
Zn	1000	$\text{Zn}(\text{NO}_3)_2$

Equilibrium – Trace Species

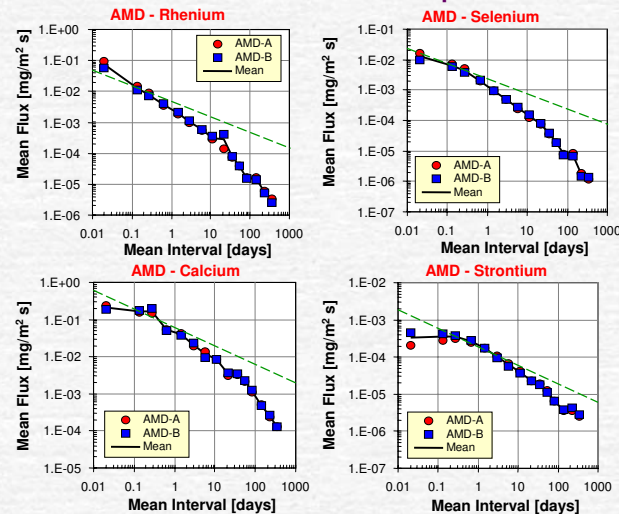


Solid-Liquid Partitioning

Comparison

- AMD – DI Water
- AMG – Synthetic Hanford Ground Water

Mass Transport Tests



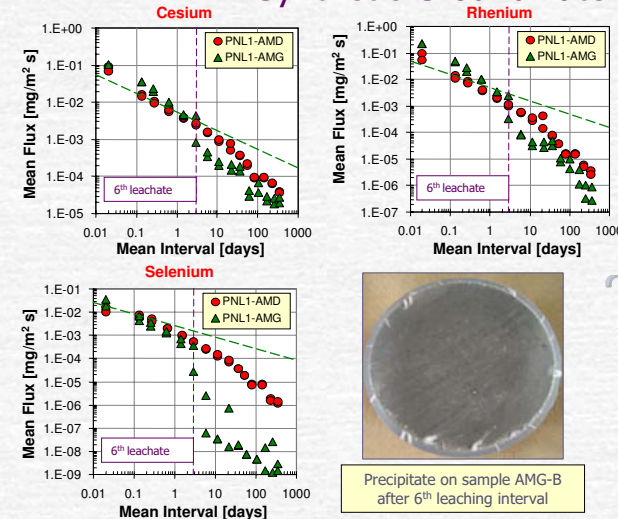
MT001 Test

- Tank Leaching in DI Water
- Constituent Flux
- Constituent Release

Comparison

- AMD – DI Water
- Flux @ constant diffusivity (green dash)

Synthetic Groundwater



MT001 Test

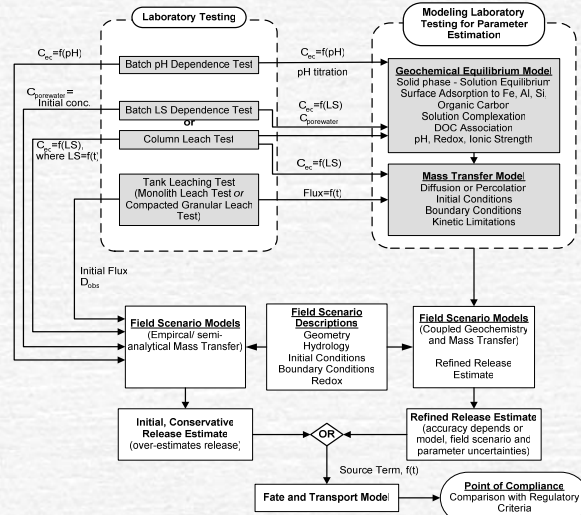
Comparison

- AMD – DI Water
- AMG – Synthetic Hanford Groundwater

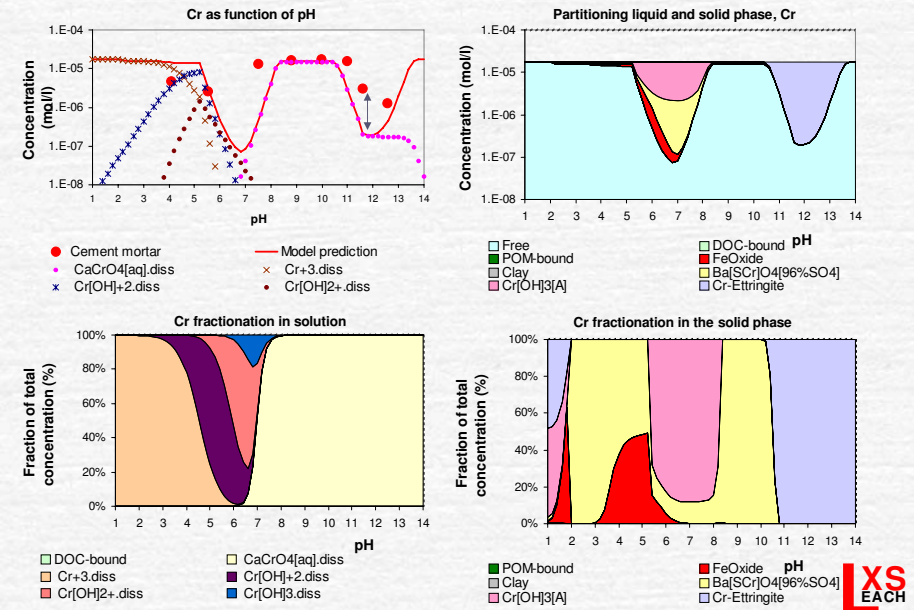
Hanford Groundwater

- CaSO_4 1.20 mmol/L
- NaHCO_3 1.04
- $\text{Mg}(\text{HCO}_3)_2$ 0.62
- CaCl_2 0.34
- KHCO_3 0.19
- $\text{Ca}(\text{HCO}_3)_2$ 0.18

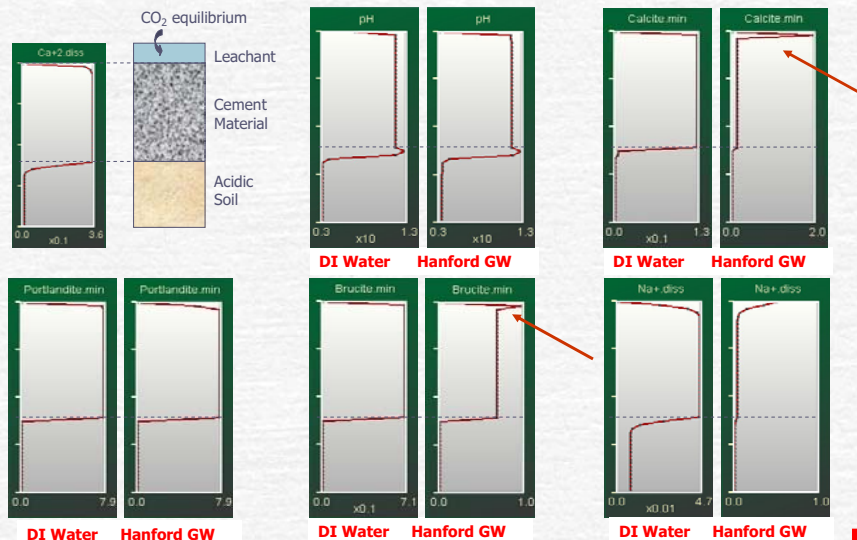
Integrated Use of Testing and Simulation



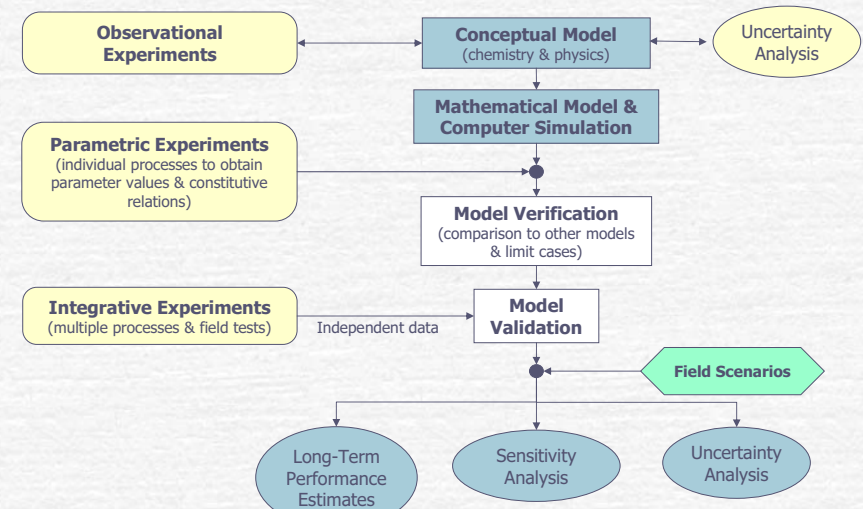
CHROMIUM SPECIATION IN MORTAR AND WATER



Leachant Simulation – Boundary Effects



Process- and Mechanism-Based Experimentation & Modeling



Key Messages

- Measure intrinsic leaching characteristics – critical test methods are defined and available, or under development
- Use geochemical speciation and mass transfer models in conjunction with management scenarios to estimate constituent release
- Use results to assess impacts, develop acceptance criteria and monitoring strategies
- Critical needs include
 - Some sub-component and integrated model parameters
 - Leaching assessment system (test methods + models) lab-to-field validation,
 - Uncertainty analysis and uncertainty propagation
 - Integration of physical degradation and leaching models

FRAMEWORK APPROACH

- Measure intrinsic characteristics**
 - Solubility and Release as function of pH (redox, DOC)
 - Solubility and Release as function of LS
 - Mass transfer rate (monolith and compacted granular)
- Evaluate release in context of field scenario**
 - External influencing factors such as carbonation, oxidation
 - Hydrology
 - Mineralogical changes
- Tiered approach**
 - Characterisation
 - Compliance
 - On-site verification

Kosson, van der Sloot, Sanchez and Garrabrants, 2002,
Environ. Engr. Sci., 19, 159-203.

Main Types of Leaching Tests

Equilibrium-based leaching tests

- Carried out on size reduced material
- Aim to measure contaminant release related to specific chemical conditions (pH, LS ratio)



Mass transfer-based leaching tests

- Carried out either on monolithic material or compacted granular material
- Aim to determine contaminant release rates by accounting for both chemical and physical properties of the material



Percolation (column) leaching tests

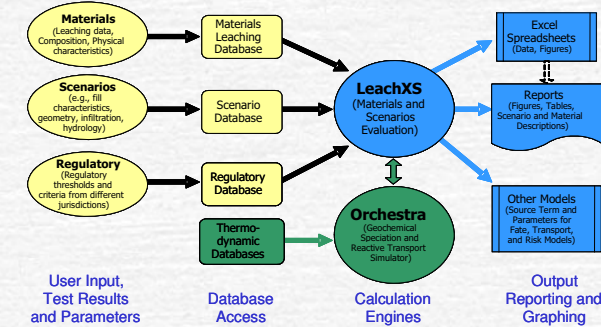
- May be either equilibrium or mass transfer rate



LeachXS – A tool for integrating experimental data, model development, parameter estimation and prediction

Software-based system for evaluating leaching

- Incorporates multiple processes and system configurations
- Data management/interpretation
- Geochemical analysis via ORCHESTRA (Meeussen, 2003)
- Database of material leaching information



Scenario Database (in preparation)

Laboratory Testing Scenarios

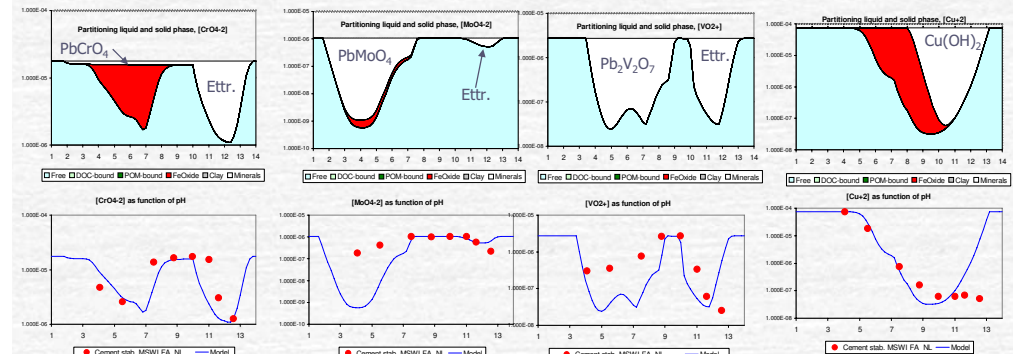
- Batch Testing of Mixtures
- Column Testing
- Monolithic and Compacted Granular Testing (Tank Leaching)

Field Scenarios

- road construction sub-base
- embankment
- landfill
- monolithic waste landfill
- drinking water pipes
- treated wood constructions
- multilayer applications
- oxidation of mining waste
- monolithic structures
- design of release from material mixtures

Geochemical modeling of stabilised waste leaching

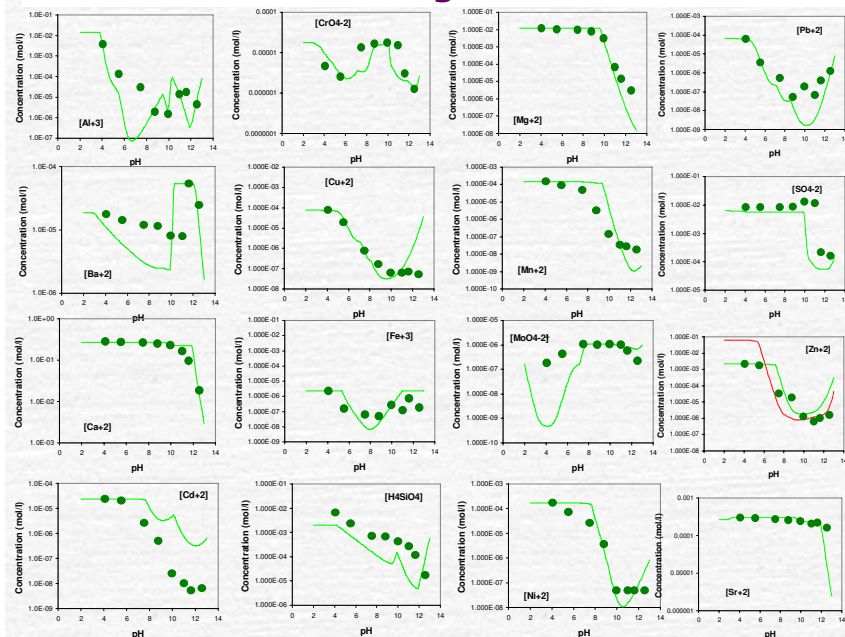
Prediction of pH dependent leaching behaviour using one set of conditions for all parameters: selected minerals, Fe-oxide and clay sorption, POM and DOC interaction. Partitioning visualised



Note: ettringite (ettr) substitution of oxyanions incorporated.

Pb availability affects prediction of Mo, Cr and V and vice versa

Geochemical modeling of stabilised waste leaching

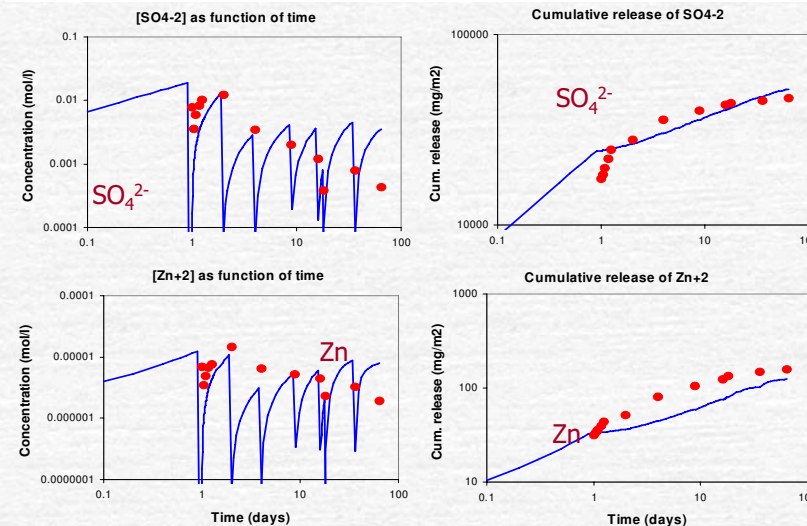


Prediction of pH dependent leaching behaviour using one set of conditions for all parameters:

selected minerals, Fe-oxide, clay, POM and DOC interaction. Ettringite substitution of oxyanions.

Cement stabilised MSWI fly ash

FULL MECHANISTIC PREDICTION OF TANK TEST RESULTS FOR A CEMENT BASED PRODUCT



Transport for a solubility controlled major element like SO_4 and a trace element Zn quite well described.

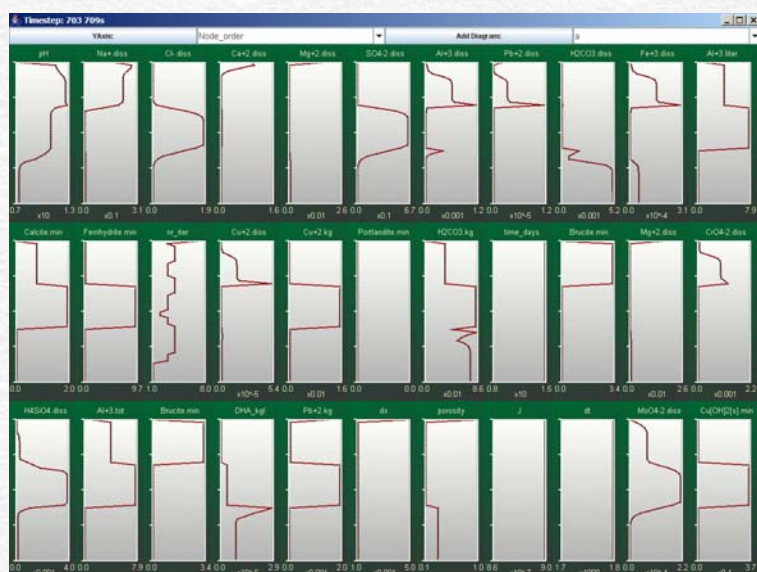
Consortium for Risk Evaluation with Stakeholder Participation

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MODELLING OF 3 LAYER SYSTEM WITH FULL CHEMICAL SPECIATION AND TRANSPORT



Cement
MSW Bottom Ash
Soil

XS
EACH

Acknowledgements

- USEPA
Office of Solid Waste
National Risk Management Research Laboratory (RTP)
Northeast Hazardous Research Center
- Consortium for Risk Evaluation with Stakeholder Participation (CRESP) with support from DOE-EM
- Recycled Materials Resource Center (UNH/FHWA)
- EU Research Program
Network Harmonization of Leaching and Extraction Tests
- Netherlands Ministry of Housing, Spatial Planning and Environment (VROM)

Consortium for Risk Evaluation with Stakeholder Participation

VANDERBILT UNIVERSITY

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Present state and perspectives of reactive transport modelling for risk assessment and leaching tests

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Laurent De Windt
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Centre de Géosciences
Equipe Hydrodynamique et Réactions
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Abstract

Reactive transport models have proven to be highly effective tools to better understand the behaviour of bio-geo-chemically reactive systems subject to hydrodynamic processes, via a wide variety of applications in different domains and at different scales. The simulation of leaching tests and, ultimately, the prediction of the behaviour of similar systems at larger scales typically requires the reactive transport modelling approach. Generally, both geochemical and hydrodynamic facets are tightly linked together and a strongly coupled modelling approach is required, solving the equations involved in bio-geo-chemistry and in hydrodynamics simultaneously. Here we propose to focus on the description of reactive transport models, emphasizing the conceptual and numerical implementation of features and processes important for leaching of mineral wastes.

1. Introduction

Reactive transport models combine microbiological and/or geo-chemical reactions with hydrodynamic processes such as water flow, diffusion and dispersion. They are increasingly used in risk assessment to understand and to predict the behaviour of reactive phases in natural or engineered systems [1]. Recently, reactive transport models have proven to be useful tools in the field of solid waste management and leaching processes in general. Leaching of solid waste forms such as *bottom ashes* in road constructions is generally adequately modelled by only a few key-processes. A model based on Brownian motion (diffusion) and simple chemistry (precipitation and/or dissolution) is indeed often sufficient to correctly model experimental results. This permits the use of a simplified *ad hoc* code [2].

Another option is to use a more general-purpose reactive transport model. Chemical reactions are considered since they affect the mobility of chemicals: retention by matrix-forming minerals, precipitation and dissolution reactions are straightforward examples. Chemistry also indirectly contributes to the migration behaviour via complexation by mobile substances (organics, colloids) and local pH and ionic strength conditions. In turn transport conditions may be altered by chemical reactions: dissolution of mineral phases may increase the porosity or lead to exposure of new mineral phases to the aqueous solution. On the other hand, precipitation may lead to clogging of part of the pore space and therefore reducing the diffusion coefficient and permeability of the medium. This feedback mechanism is particularly important at very reactive interfaces such as are found between cement and clays [3].

A major advantage of the latter option is that modelling concepts and the associated database are readily transposed to other scales, with possibly more complex boundary conditions and additional chemistry to deal with. As the same model can deal with batch-, flow-through and column experiments, we preserve internal consistency and avoid error-prone transcription of data between intrinsically different codes. This is even more pertinent when moving from laboratory to field scales. For example, *in situ* conditions may require an unsaturated flow model or a meteoric upper boundary condition: the physico-chemical processes retained to simulate the leaching process in laboratory conditions still remains valid and can be used under non-saturated conditions – provided, of course, that this option is properly and consistently implemented.

- the distribution coefficient lumps a certain number of system parameters which are not constant when scaling up. Among others, the value of K_d depends on the water-exposed surface area and solid/liquid ratio, which change significantly when moving from unconsolidated matter to porous or fractured media;
- variable chemical conditions have a sometimes significant impact on the distribution coefficient, due to e.g. aqueous complexation, competition effects and redox processes [1].

Instead, $\bar{C}$ should be evaluated by an approach based on phenomenological processes, possibly surface complexation and/or cation exchange, and appropriate models accounting for e.g. electrostatic effects, Donnan potentials and water-accessible surface areas. This approach may require parameter values that are not necessarily provided by the available experimental data. Recent thermodynamic databases, however, provide reasonable estimates for many parameters. Others need to be estimated, which introduces the notion of uncertainty – only rarely taken into account in risk assessment studies but feasible and necessary.

Kinetics add another level of complexity to reactive transport models. Most experiments require a kinetic approach to correctly simulate mobilisation of metals due to dissolution. A simplification to account for kinetic inhibition of the expected thermodynamic equilibrium is to reduce the thermodynamic formation constant of the solid phase [2]. This may lead to an acceptable fit of the experimental data but introduces the risk of underestimating the mobile fraction if the database is used in another context or at larger time scales – e.g. *in situ*. Moreover, kinetics are the basis of modelling microbial processes. Using a trustworthy thermodynamic database in combination with a plausible kinetic inhibition process is expected to perform much better at different timescales.

3. A propos: the HYTEC model

HYTEC is a reactive transport model integrating a wide variety of features and options, which, after a decade of development, has evolved to a versatile simulation tool [9]. Bio-geo-chemistry is provided by the module CHESSE. Accordingly, the model accounts for many commonly encountered processes including interface reactions (surface complexation with electrostatic correction, cation exchange), precipitation and dissolution of solid phases (minerals, colloids), organic complexation, redox and microbial reactions, etc. All reactions can be modelled using a full equilibrium, full kinetic or mixed equilibrium-kinetic approach. Thermodynamic data is taken from the database developed by the Common Thermodynamic Database Project (CTDP) [12].

The hydrodynamic module of HYTEC is adapted for hydrodynamic conditions commonly encountered in the laboratory or in the field. Among others, the code allows for unsaturated media, variable boundary conditions, sinks- and sources. HYTEC searches for an accurate solution to the multi-component transport problem using an iterative, sequential, so-called *strong coupling scheme*. Strong coupling permits variable hydrodynamic parameters in function of the local chemistry. For example, the porosity of a porous medium reduces after massive precipitation of neo-formed mineral phases, which modifies the water flow paths and transport parameters, e.g. diffusion coefficients: HYTEC solves this interdependency accurately, which makes the tool particularly useful for e.g. cement alteration at long timescales (e.g. storage of waste and performance assessment).

The application domains and scales of HYTEC are numerous, as illustrated by Figure 1. Simulation of cement hydration requires extremely short space (and time-) scales. Degradation of materials such as ashes, concrete and cement generally implies a modelling unit at intermediate scales, typically in the order of a litre. Waste dumps, (e.g. mine tailings), deep underground radioactive waste disposals and sequestration of green house gases are simulated at much larger time and space scales, as illustrated by the figure.

The drawback of using fully fetched reactive transport models is that, in an attempt to correctly describe a large number of simultaneously occurring processes, they tend to become increasingly complex. Consequently, verification and validation of the codes becomes an issue of concern. Moreover, their use in decision-making and critical or sensitive application domains require a rigorous and permanent verification and confidence-building process. The development of HYTEC, for example, is governed by a French national consortium, which guards against non-regression and guides the development in function of industrial and scientific needs.

Reactive transport models are often evolutions of either a hydrodynamic transport model (enriched with chemical processes) or a bio-geo-chemical code (enriched with hydrodynamic processes). Examples of the first class of models are SHEMAT [4], MCOTAC [5] and RT3D [6]. Examples of the second class are e.g. PHREEQC [7] and PHAST [8]. Some codes are developed *from scratch* for coupling purposes: HYTEC [9], ORCHESTRA [10] and CRUNCH [11] are only a few examples of recent instances. They all deal with the major features and processes involved in chemistry and hydrology, but differ in specific options, databases, precision and numerical solution methods – not to mention the user interface (ease of use). Therefore, the choice of reactive transport model will depend on the application domain of interest.

2. Important features and processes

Reactive mass transport in a porous medium is generally modelled by the usual form of the advection/dispersion equation:

$$\frac{\partial(\theta C_j)}{\partial t} + \frac{\partial(\theta \bar{C}_j)}{\partial t} = \nabla \cdot (D \nabla C_j - U C_j) + q(C_j)$$

where θ denotes the water-content of the medium, C_j is the mobile and $\bar{C}_j$ the immobile concentration of species j , such that the total concentration is $\bar{C} = C + \bar{C}$. D includes diffusion and dispersion and U is the filter flow vector. The right-most term represents a local, flow-independent source or sink. Assuming laminar, isothermal and incompressible flow in porous media, the velocity field is obtained by Richard's equation that, under saturated conditions, reduces to the well-known equation proposed by Darcy with θ being equal to the porosity of the medium. This equation is readily solved using appropriate numerical techniques. For multi-component reactive transport, the finite-volumes approach has some interesting advantages with respect to e.g. finite elements or differences [9].

Bio-geo-chemistry defines which fraction of an element is mobile or immobile. If, for example, we consider a medium which contains lead, the mobile fraction is the sum of all ionic Pb species (Pb^{2+} , PbOH^+ , $\text{PbCO}_3(\text{aq})$,...) and the immobile fraction is the sum of all mineral Pb species (cerussite, litharge,...) plus the sorbed fraction, if processes like surface complexation and cation exchange are involved. A speciation model is required to precisely establish the immobile fraction, but also provides other useful information: e.g. some aqueous complexes are more bio-available than others and therefore more relevant for risk assessment.

Often, $\bar{C}$ is calculated using a simple linear relationship, $\bar{C} = K_d C$, with K_d being the retardation coefficient. Within the transport equation, the K_d leads to a linear retardation-coefficient, applied to the diffusion, dispersion and advection terms. This approach should be used with care for the following reasons:

- the fundamental principle of mass conservation is not respected: the total amount of species C_j is not fixed but a function of the mobile fraction;

Recent research with HYTEC is focused on the long-term stability of cement and concrete. Concrete is often simulated by a typical CEM-I cement including mainly portlandite, CSH

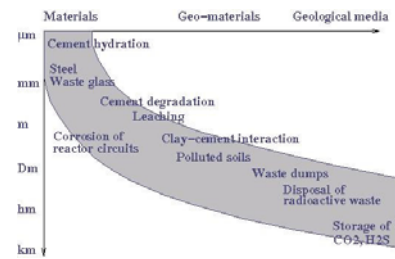


Figure 1. Application domains of the reactive transport model HYTEC. Most applications are carried out within the framework of the Reactive Transport Consortium PTG.

(calcium-silicate hydrate with a high Ca/Si ratio) and small concentrations of ettringite and calcium monosulfo-aluminate. More sophisticated models for cements are sometimes used, including sorption on primary or secondary CSH phases, carbonation and sulfatation of the material. These features, as well as the strong coupling approach as outlined above make HYTEC particularly useful for the modelling of long-term leaching of solidified wastes [13].

4. Conclusion and perspectives

Risk assessment, waste management and fundamental scientific research require a modelling approach, which covers all scales involved. Today's reactive transport models provide a solution to this problem, allowing to simulating numerous, sometimes tightly interwoven processes in an accurate manner. They become predictive tools, applicable to long-term dynamic leaching of wastes, to performance or risk assessment of waste repositories and to related application domains.

Although the application of simplified models is seemingly justified by good fits to experimental data, they contain the potential danger of wrongly predict the system behaviour at larger scales. For example, replacing kinetic inhibition by lowering the thermodynamic formation constant of the waste matrix may lead to an underestimation of contamination if extrapolated to larger time scales. Similarly, K_d coefficients should be used with care or avoided if possible. Instead of simplifying the system, it is preferable to use a fully fetched reactive transport model, even if the latter requires more parameters than actually obtainable by the experimental data: in that case, they can be estimated. Unknown or estimated parameters values are useful since they allow us to quantify, to some extent, the uncertainty involved in the simulations.

With respect to uncertainty, thermodynamic database development remains one of the key issues of the reactive transport problem. The increase in the use of chemical models and the tremendous amount of work involved in developing and maintaining an operational thermodynamic database require new methods, based on collaborative efforts of the international scientific community. Databases should not only contain thermodynamic values, but uncertainty estimates as well. Also, further progress is required on the topic of sorption

processes (sorption databases), kinetic data, the role of colloids in natural systems and microbial activity, the latter playing an important role in virtually all subsurface systems.

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” MODELS FOR IMPACT EVALUATION ON LANDFILL- ASPECTS FOR PROPER MODELLING ”

Margareta Wahlström
BRGM-workshop 19.-20.10.2006, Paris



VTT PROCESSES

OUTLINE OF PRESENTATION

- ♦ Background to work
- ♦ Drivers
- ♦ Goals in modelling
- ♦ Important aspects
- ♦ Recommendations



VTT PROCESSES



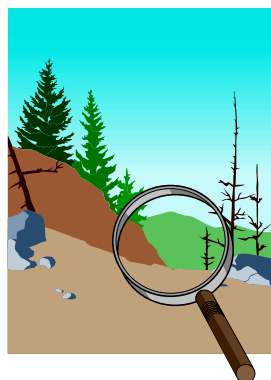
Project: MODELS FOR IMPACT EVALUATION ON LANDFILL- ASPECTS FOR PROPER MODELLING

Financier: Nordic Innovation Centre

Partners:

- ♦ VTT Processes, Finland (co-ordinator)
- ♦ DHI, Denmark
- ♦ SGI, Sweden

Timetable: 2004-2005



VTT PROCESSES

OBJECTIVES OF NORDIC PROJECT

- ♦ to discuss requirements for proper modelling (steps to be included, tools, selections of models, documentation, transparency etc)
- ♦ to address possibilities and limitations in modelling and own experience from the modelling
- ♦ to point out key aspects to be considered in modelling
- ♦ to present examples of modelling results
- ♦ to give a common approach for modelling



VTT PROCESSES

DRIVERS

EU Landfill directive 1999/31/EC: landfill classes and landfill constructions

- ✓ Deviation in landfill construction (bottom liner, top liner)
- ✓ Deviation in disposal conditions (sensitivity of surroundings)



Council Decision 2003/33/EC: criteria and procedures for the acceptance of waste at landfills

- ✓ Need for 2-3 times higher limit values
- ✓ No limit values in EU regulation

Development of National Regulations for use of industrial by-products in earth constructions

- ✓ Material specific criteria for specified utilisation option

Development needs in CPD/ER3

- ✓ National regulatory values for specified scenarios

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IMPACT EVALUTION – Goals

- Estimates of release at selected point of compliance (e.g. time dependent release, total burden, water flows)
- Comparison of release in selected scenarios
- Information on influence of material properties and environmental conditions on release



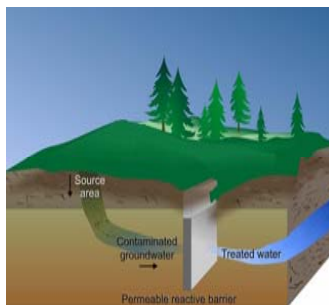
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IMPACT EVALUTION – Tools

Available modelling tools:

- geochemical modelling linked to waste characterization (prediction of long term behaviour)
- models for estimation of water flows/balance
- transport models for estimation of transport by water to surroundings



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END-USERS OF MODELLING RESULTS

End-users	Goals with modelling (examples)
Scientists	Explanations/verifications of processes/reactions
Waste producers	Selection of management options
Landfill operators	Comparisons of treatment techniques
Waste processing companies	Development of stabilisation recipes
Legislators	Development on utilisation criteria
Waste authorities	Risk assessment (impact evaluation)



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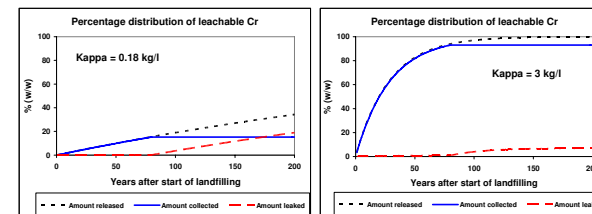


CHALLENGES

- ✓ discrepancies between expectations of end-users and outcome from modelling – what do my results stand for?
- ✓ misuse of modelling results due to ignorance (problems with vocabulary)
- ✓ small & specific waste streams (no references, no frequent modelling needs)
- ✓ validation of modelling results
- ✓ approach in modelling (definition of acceptable risk level, inclusion of on-site background concentrations in model, soil properties)
- ✓ suitability of models for arctic conditions
- ✓ applicability to my case?
- ✓ do I need prediction of long term behaviour for the modelling?



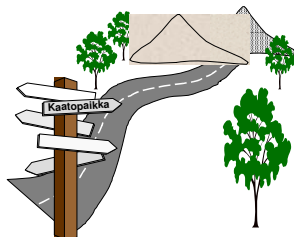
EXAMPLE: Influence of kappa on the source function (in CSTR-model)



(ref. Hjelmar, 2005)

IMPORTANT ASPECTS IN MODELLING

- ♦ Design of a conceptual model based on available basic information
- ♦ Identification of the critical exposure route
- ♦ Definition of accepted risk level or reference values
- ♦ Selection of appropriate modelling tool (transparency, simple contra sophisticated model)
- ♦ Justification of input data and assumption, including evaluation on how choices affects end-results (sensitivity analysis)
- ♦ Knowledge on legal restrictions (e.g. hazardous waste management)



REQUIREMENTS FOR PROPER MODELLING

Phase:

1. Estimation of release from the waste deposit
2. Estimation of the transport in the unsaturated zone
3. Estimation of the transport to the surface water
4. Estimation of the transport with groundwater to point of concern (POC)
5. Geochemical modelling Estimation of long term behaviour of deposited waste

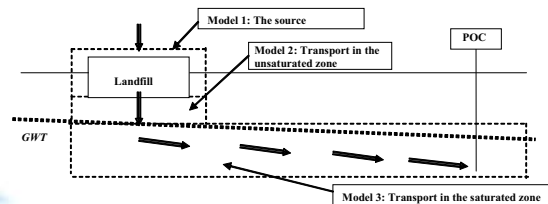
Requirements for proper modelling

- reliability of laboratory leaching data
- realistic water flow estimates
- good knowledge of model requirements
- selection of proper model tools based on available input data
- proper documentation
- see point 2
- see point 2
- good knowledge of chemical reactions
- experience of model applicability
- information of species included in database
- proper documentation

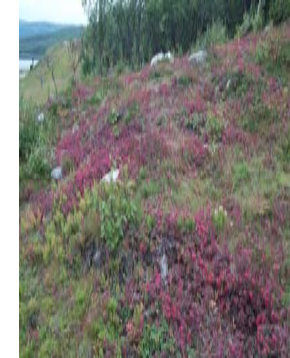


RECOMMENDATIONS

- ♦ A guideline with descriptive examples needed
- ♦ If possible, a recommendation on a basic approach (the so called TAC-methology was recommended in the Nordic project)
- ♦ Competence of modellers with sufficient model knowledge, references (most crucial)
- ♦ Also discussion on supplementary information needed (e.g. total load and dust emissions)



VTT PROCESSES



"Modelling results should be used to help in decision making. Results do not stand for true value. They only show an anticipated release under certain assumptions"

VTT PROCESSES



THERMODDEM: a thermodynamic database for waste materials

**Philippe Blanc, Arnault Lassin, Céline Nowak,
André Burnol, Patrice Piantone**
BRGM, Process & Environment Division, Orléans

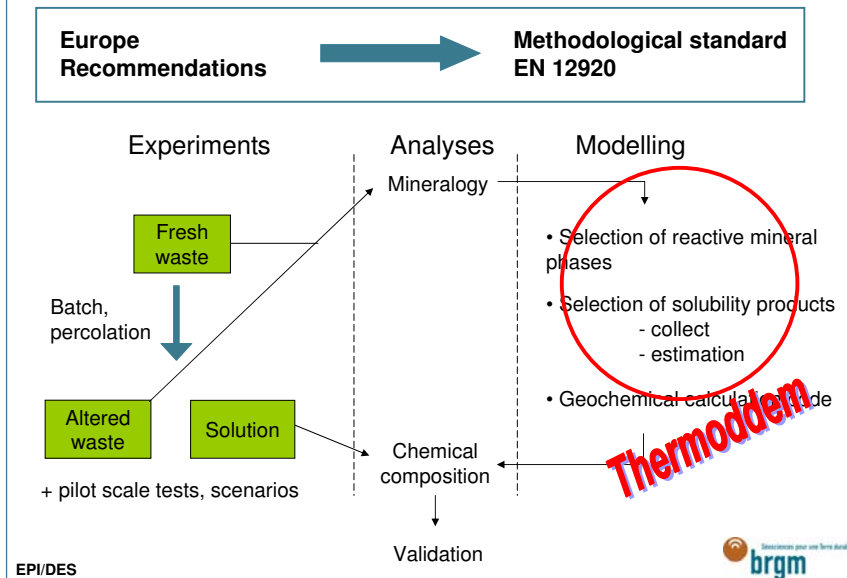




Agence de l'Environnement et de la Maîtrise de l'Energie

jeudi 14 décembre 2006

Context



EPI/DES

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> 2

The ideal database... for geochemical modelling (1/3)

> Valid for many contexts

- Behaviour of pollutants
 - Reuse of solid waste as building materials
 - Polluted sites & soils (natural attenuation)
 - Waste storage scenarios
- Improvement of industrial by-products management
- ... other than waste materials



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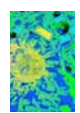
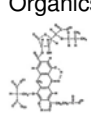
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> 3

The ideal database... for geochemical modelling (2/3)

> This implies technical capabilities

- Numerous elements
 - Aqueous

 Diluted
Saline
 - Solids & gases

 Minerals
Surfaces
Kinetics
 - Organics

- Temperature 
- Quality
 - Thermodynamic data as reliable as possible

Critical selection Referenced sources Internal consistency

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> 4

The ideal database... for geochemical modelling (3/3)

> A living database

- Help for modellers
 - mineralogical/geological information
 - Output format (PhreeqC & others)
- Modifiable
 - Individual phases data → reaction data
 - Internal consistency preservation
- Continuously implemented
- Access on the Internet
- Information on data selection (links to documentation)

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> 5

State of the art

> Heterogeneity of bases as a function of uses

Alloys
Ex : SGTE

Numerous elements
Few minerals
No aqueous species
Critical review
T°

Nuclear waste storage
Ex : NEA

RN dedicated
Critical review
T°

Metamorphic
Ex : Gottschalk 97

Few elements
Few minerals
No aqueous species
Consistent
T°,P

Water-rock interactions
Ex : Ilnl.dat

Numerous elements
Numerous minerals
Heterogeneous
T° Problem

Environmental, s.l.
Ex : CTDP

Numerous elements
Numerous minerals
Critical review
T° Problem?
Living data base
Ongoing project

What about
Enrichment, up-dating?
Sources?
Data Selection?
Waste materials?
Help for modellers?

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> 6

What's inside THERMODDEM?

> The core of the thermodynamic database

- CODATA
 - International reference for 34 elements, & a few simple compounds
- Supcrt92 (slop98)
 - Many elements ~90, minerals & aqueous species + T,P dependence
- Robie & Hemingway
 - Minerals & gases, calorimetric data
- US Bureau of Mines
 - Minerals & gases, calorimetric data

&

- Scientific literature
- Feedback from projects & partners

> The geological/mineralogical database

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> 7

A rapid view

THERMODDEM
Thermodynamics database devoted to the modelling of waste minerals alteration

Mineral

Nomenclature
Name of mineral: CHALCEDONY
Formula: SiO2
family:

Other members
[No other member in the family.]

Polymorphs
AMORPHOUS-SILICA (SiO2)
COESITE alpha (SiO2)
COESITE beta (SiO2)

Mineralogy
Space group: See Quartz, Moganiite, Triclinic, Monoclinic, - Prismatic, H.M. Symbol (230) Space Group: 12h

Data class
See Quartz, Moganiite, 75.1.4.2 (75) Triclinic, H.M. Symbol (230) Space Group: 12h, coordinated Si (75.1.4) Data Group:

Occurrence & geological context
Stable in very low temperature environments, even sedimentary mineral. Traditionally defined as a fibrous cryptocrystalline variety of Quartz, more recently, it has been shown that much Chalcedony is a mixture of Quartz and Moganiite, another Silica mineral.

Alteration & pathway
Confined medium:
Weathering:

Thermodynamics
Mineral properties
 ΔG_f° : -854 091 J/mol
 ΔH_f° : -859 150 J/mol
 S° : 41.34 J/mol K
Quality (1 to 5):
 M_{SiO_2} : 60.084 g/mol
 V : 22 680 cm³/mol
Stability range
Very low temperature environments

Test (coherence): -32 J/mol
Reaction properties
SiO2 = 1SiO2
Van't Hoff
Log K: -9.73
 ΔH_r° : 31 409 J/mol

Analytic
Log K = A + BT + CT² + D Lnt + ET²
A: -771.22
B: -40.89
C: 50.285 95
D: 269.47
E: -3.711 522 63

T (°C)	0	25	60	100
Log K	-4.34	-3.73	-3.23	-2.86
Log K	-2.53	-2.27	-2.05	-1.88

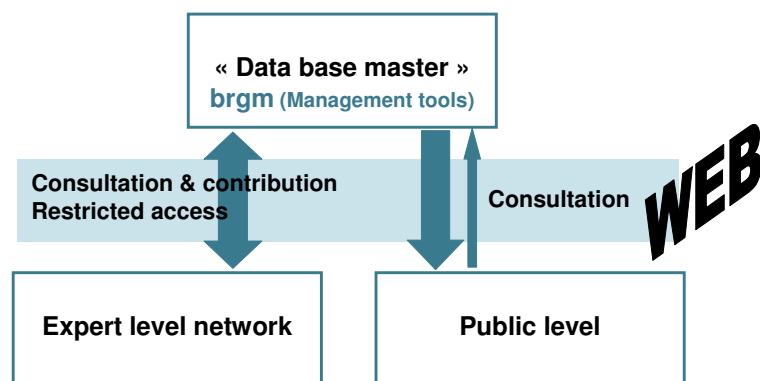
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Management of the database



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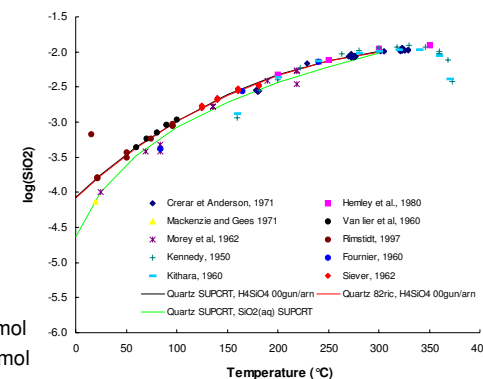
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An example: Silicon

1/2

> New works on quartz solubility (1997 to 2000)

- Formerly: $1.0 \cdot 10^{-4}$ mol/l
- New data: $1.8 \cdot 10^{-4}$ mol/l



> Consequences on:

- ΔG_f° for H_4SiO_4
 - Old value: -1307.69 kJ/mol
 - New value: -1309.18 kJ/mol
- temperature dependence of the equilibrium constants for Si-bearing complexes and minerals

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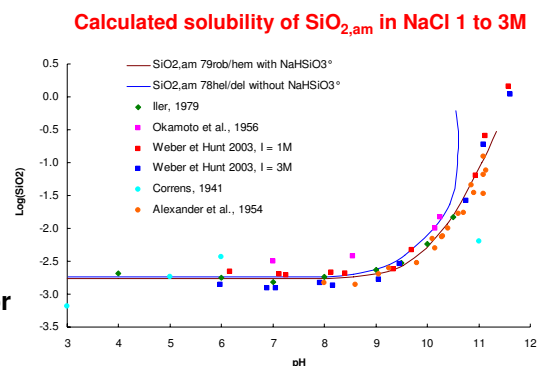
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An example: Silicon

2/2

> Validation of the set of Si-bearing complexes vs amorphous silica solubility

> Importance of the NaHSiO_3 complex for high pH solutions



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> 11

Conclusions

1/2

Done
Ongoing
In project

> Technical capabilities

- Numerous elements



- Temperature

- Quality
 - Thermodynamic data as reliable as possible

Critical selection Referenced sources Internal consistency

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> 12

Conclusions 2/2

Done
Ongoing
In project

> Living database

- Help for modellers
 - mineralogical/geological information
 - Output format (PhreeqC & others)
- Modifiable
 - Individual phases data → reactions data
 - Internal consistency preservation
- Continuously implemented
- Access on the Internet
- Information on data selection (links to documentation)

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> 13

Thank you

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> 14

Complements

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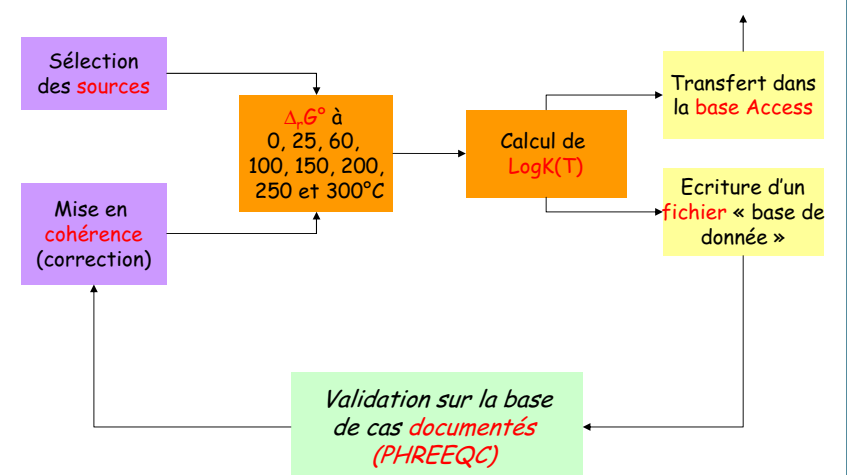


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> 15

Construction : schéma conceptuel

WEB OU PARTENAIRES



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> 16

En cours et perspectives

> Réalisé

- 340 phases minérales sélectionnées
- 1400 complexes aqueux HKF (différentes sources)
- Outil de gestion Excel
- Validation base ciment

> En cours

- Finalisation de l'outil WEB
- 3000 minéraux (10 jours)
- Sélection de la base HKF
- Validations en cours (feldspath, Pb, phosphates, carbonates)

> Perspectives ANDRA

- Assurer la cohérence entre Thermochimie et Thermoddem
- Intégrer les phases du systèmes fer-argile
- Compléter la base ciment/argile avec plus de zéolites

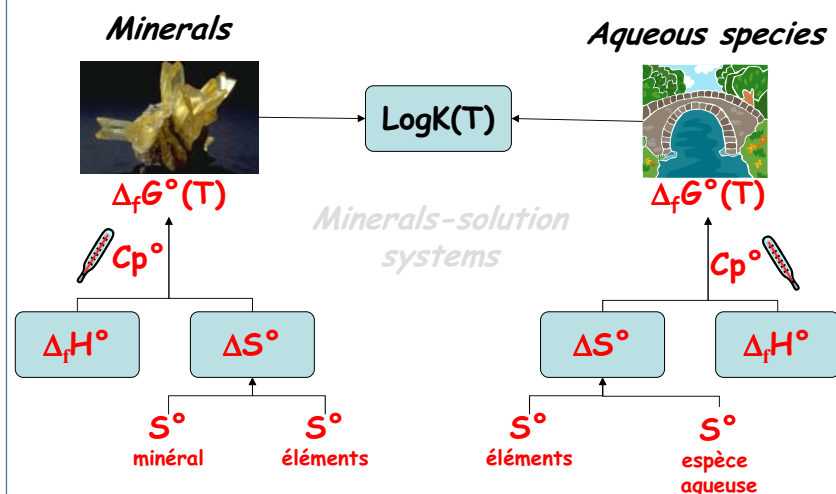
Construction 2 : la question des sources

Phases	Référence	S° (J/mol/°K)	Travaux de
Rutile	CODATA	50.6 ± 0.3	Mah (1957) Humphrey (1951)
	JANAF98	50.29 ± 0.17	Mah (1957)
	Robie95	50.6 ± 0.6	CODATA
	HSC 5.1	50.29	Barin 93
	Naumov74	50.37 ± 0.2	Kelley 1961
	Wagman82	50.0	
Anatase	Slop98	50.29	Robie et al., 1979
	Barin73	50.33	JANAF75
	Pankratz82	50.37	Shomate (1947)
	JANAF98	49.91 ± 0.3	Shomate (1947)
	Wagman82	49.92	
	Robie95	49.9	JANAF85
	HSC 5.1	49.91	Barin 89
	Naumov74	49.92	Kelley 1960
	Barin73	49.92	JANAF75
	Pankratz82	49.92	Shomate (1947)

- Peu de références à des travaux expérimentaux
La traçabilité est très variable.

- Les données sont mesurées pour plusieurs phases par le même auteur : la cohérence entre propriétés et entre minéraux peut être discutée

Nature of thermodynamic data





Coupled modelling of leaching tests and environmental processes applied to stabilized waste

Laurent De Windt, Rabia Badreddine

Context and objectives

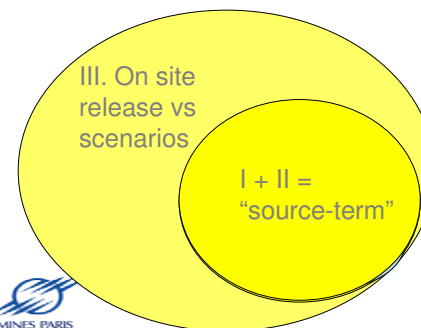
➤ Environmental impact assessment of waste disposal or recycling scenarios

- Dynamic leaching tests to better characterize the waste long-term evolution
- Understanding of leaching mechanisms to extrapolate the laboratory results to disposal and environmental conditions

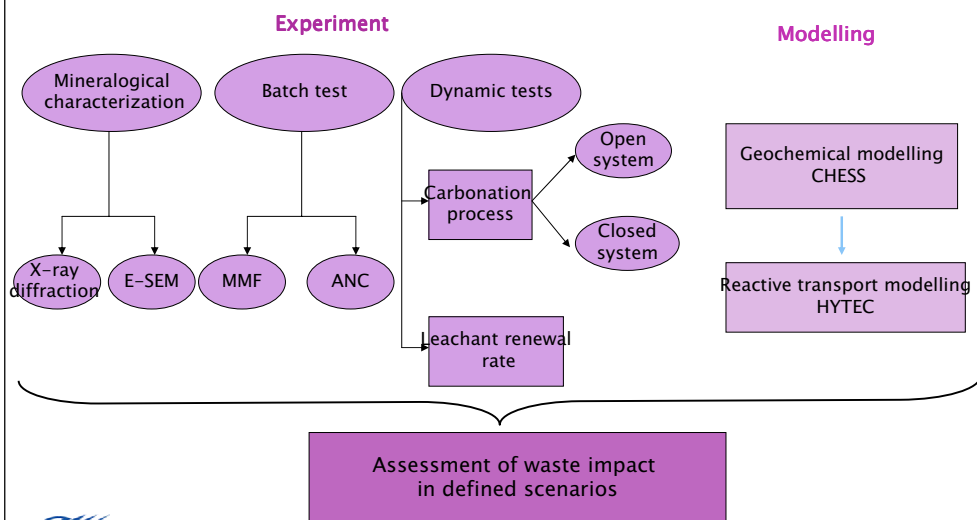
➤ Needs for a "common" modelling approach and code applied to different scales, as mechanistic as possible

- Reactive transport codes are good candidates

- I + II: *Waste Management (2006), in press*
- III: *J. Hazardous Mater. (2006), in press*



Source-term characterization



Solidified/stabilized waste



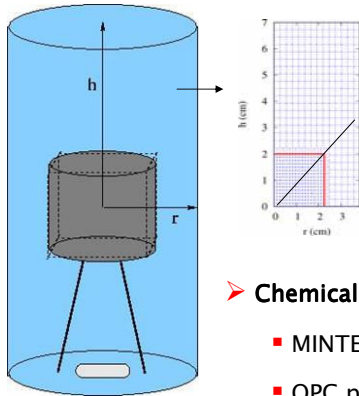
➤ Solidification recipe:

- 1 / 4 CEM-I (OPC)
- 3 / 4 siliceous sand
- Pb (1%)

➤ Porous monolithic material:

- $4 \times 4 \times 4 \text{ cm}^3$
- $\omega \sim 0.15$
- $Deff \sim 3 \cdot 10^{-12} \text{ m}^2/\text{s}$

Modelling features



➤ Reactive transport code HYTEC:

- 3D-cylindrical geometry (REV)

$$\frac{\partial \omega c_i}{\partial t} = \nabla(D_e \cdot \nabla c_i) - \frac{\partial \omega c_i}{\partial t}$$

- feedback of chemistry on ω and D_e

$$D_e(\omega) = D_e(\omega_0) \left(\frac{\omega - \omega_c}{\omega_0 - \omega_c} \right)^m$$

- closed (or open) conditions

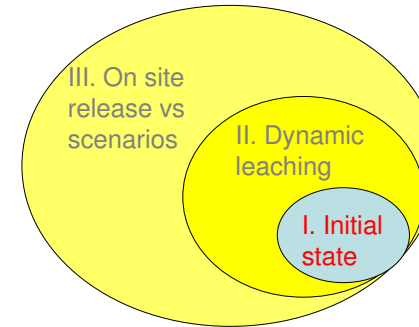
➤ Chemical model:

- MINTEQA2 + cement phases (+ sorption)
- OPC pore water chemistry (pH ~ 13.3)
- CSH, portlandite, ettringite, Friedel's salt, hydroxalite
- Pb in substitution in CSH 1.7



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Stage 1



➤ Needs for a “common” modelling approach and code applied to different scales, as mechanistic as possible

- Reactive transport codes are good candidates

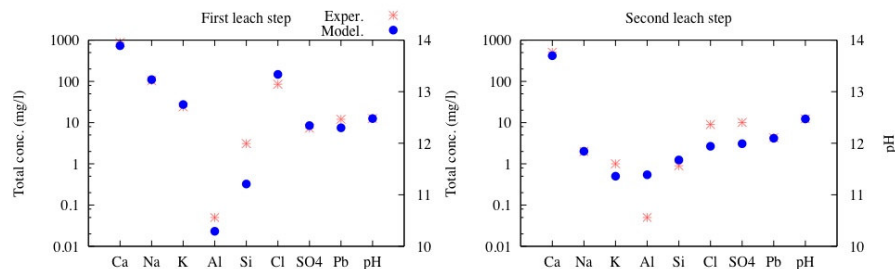


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Porewater and MMF test

L/S = 10

L/S = 50

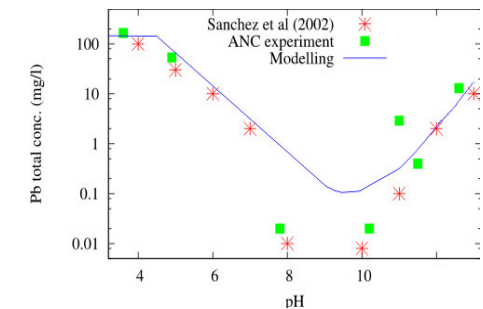
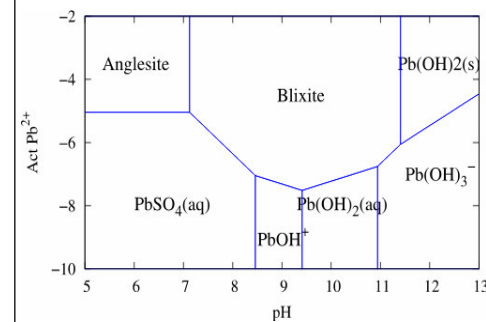


- Local thermodynamic equilibrium assumption with initial solid phases +
Na, K, Cl (almost) conservative and adjusted from the MMF batch tests
- Fairly to very good experimental/modelling agreement
- Extrapolation to ∞ L/S gives pore water chemistry



INERIS

Lead solubility vs pH and ANC test



- Good at very good agreement except for the lowest concentration, in particular the amphoteric properties
- Pb solubility would be controlled by hydroxide-like complexes and solid phases at alkaline pH and closed conditions, no matter Pb is substituted or sorbed on CSH ?



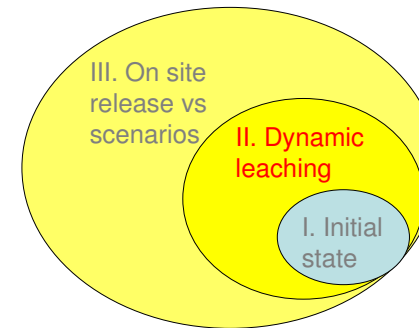
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Calculated pore water chemistry

Calculated chemistry of pore water with considering the sorption of Na on CSH phases.

pH	13.3	
Na ⁺	8 800	mg/l
K ⁺	4 100	mg/l
Ca ²⁺	64	mg/l
Pb ²⁺	57	mg/l
Al ³⁺	0.08	mg/l
H ₄ SiO ₄	99	mg/l
Cl ⁻	5 050	mg/l
SO ₄ ²⁻	1 250	mg/l

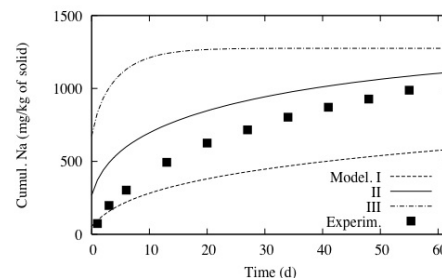
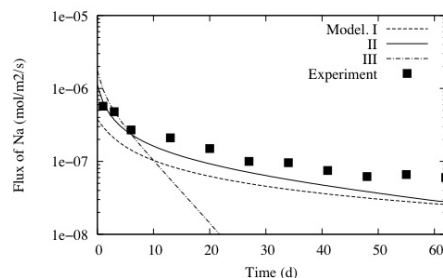
Stage 2



➤ Needs for a “common” modelling approach and code applied to different scales, as mechanistic as possible

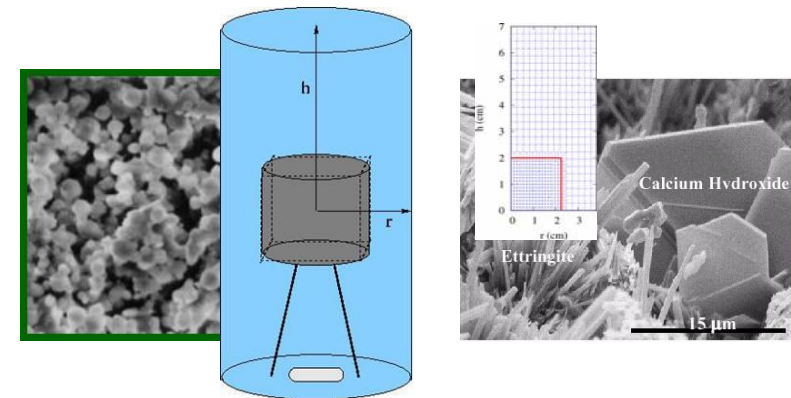
- Reactive transport codes are good candidates

Sodium evolution and flux during reactor leaching



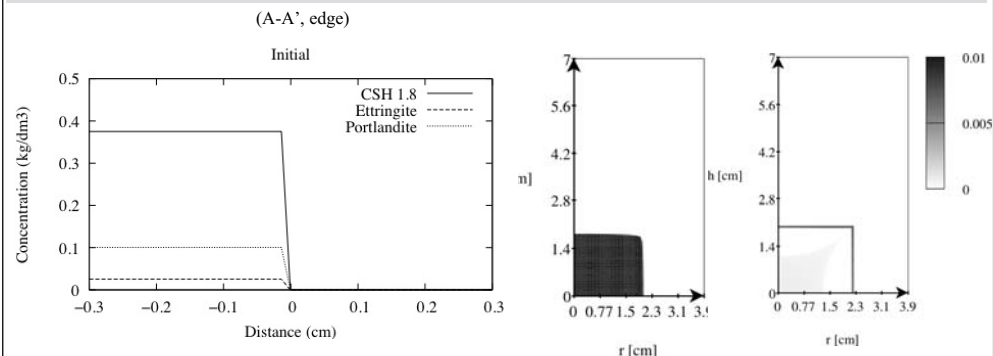
- conservative diffusion-controlled assumption globally applicable
- > 99% of the initial total inventory is leached for 250 ml/h
- (+ slight effect of the renewal leachant rate)

What's the surface of a porous media



- ⇒ Elementary Volume Representation of the interface rather than a geometrical surface
- ⇒ Equilibrium approach, diffusion-controlled (in a first step)

Mineralogical evolution



Two main distinct main fronts
(slightly) speeded up by porosity opening

AFm dissolution and hydrotalcite precipitation



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Element release vs grid refinement

Sensitivity of the calculated cumulative releases (mg/kg of solid) with respect to the refinement of the calculation grid.}

Node size (m)	Na	K	Ca	Pb	H ₄ SiO ₄	Cl	SO ₄
2.5x10 ⁻³	1 100	285	1 290	11	4.5	670	80
1.25x10 ⁻³	1 100	285	2 750	35	6	760	80
6.25x10 ⁻⁴	1 100	285	4 585	54	13.5	760	96
3.1x10 ⁻⁴	1 100	285	5 000	63	58	715	125
1.5x10 ⁻⁴	1 100	285	5 000	67	250	715	150
1.5x10 ⁻⁴ (*)	1 100	285	9 200	132	2 050	715	240

Experimental 1 050 350 15 840 70 12 750 500 245

(*) This simulation takes into account the feedback of mineralogical evolution on porosity and diffusion coefficient.

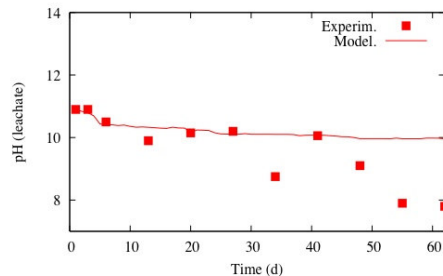
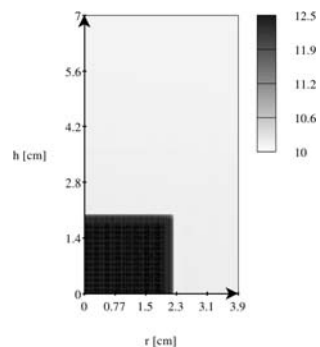


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pH evolution during reactor leaching

in the monolith

in the reactor vessel

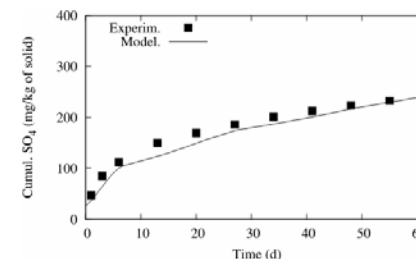
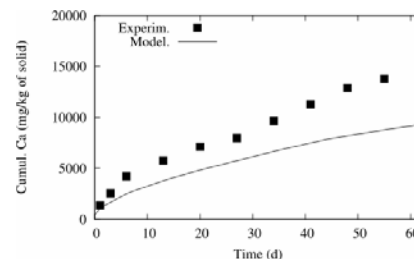


- pH profiles can be calculated in the monolith itself (function of Na-K diffusion and portlandite dissolution)



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Calcium evolution and flux during reactor leaching

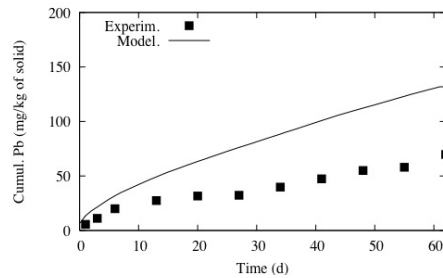


- Essentially solubility-controlled (monolith "surface" dissolution)
- Initial total inventory almost unchanged



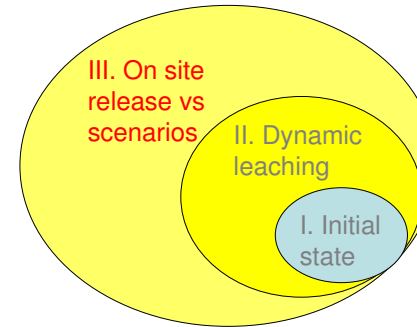
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Lead evolution and flux during reactor leaching



- Diffusion and solubility controlled, Pb/Ca flux ratio ~ 0.001
- Less than 0.5% of the initial inventory is leached for 250 ml/h

Stage 3



➤ Needs for a “common” modelling approach and code applied to different scales, as mechanistic as possible

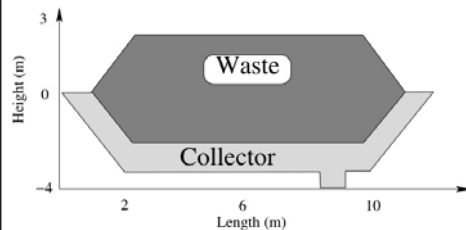
- Reactive transport codes are good candidates

Storage scenario with undamaged waste



Effective infiltration rate = 330 ml/a

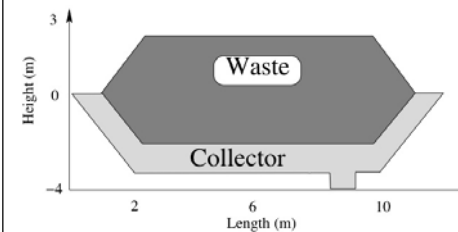
Thermal stress might induce micro to macro cracks.
How this would impact on toxic waste release?



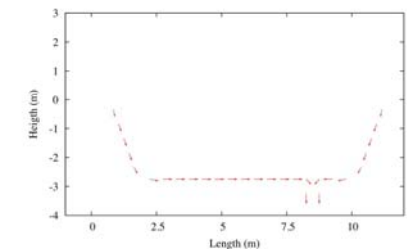
- Test-case A = undamaged monolith ($\sim 1 \text{ m}^3$)
- Test-case B = macro-fractures
- Test-case C = micro-crack network

$$\frac{\partial \omega c_i}{\partial t} = \nabla \cdot (D_d \nabla c_i - c_i U) - \frac{\partial \omega \bar{c}_i}{\partial t} + \text{dual porosity}$$

Storage scenario with undamaged waste

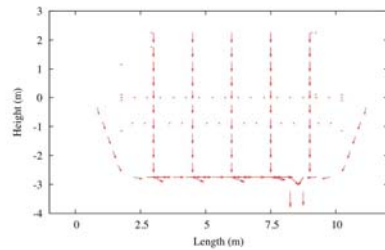


Test-case A = undamaged monolith

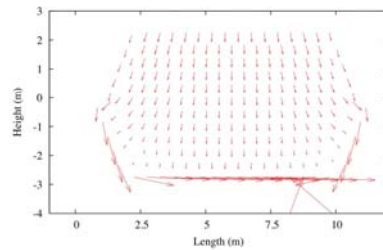


Storage scenario with fractures or cracks

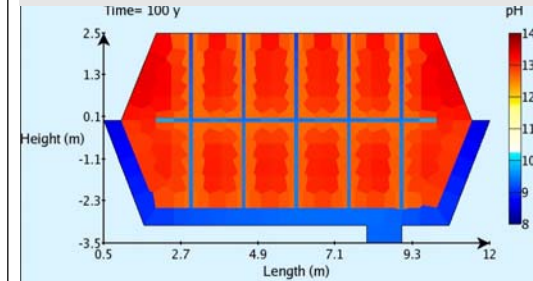
Test-case B = macro-fractures



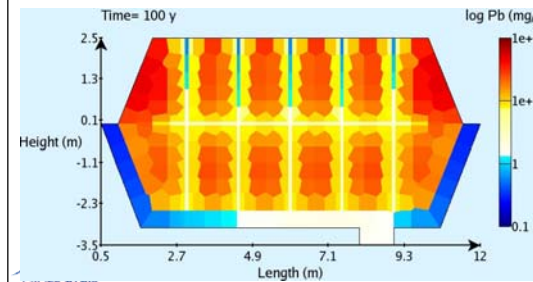
Test-case C = micro-crack network



pH and Pb aqueous conc. evolution (case B)

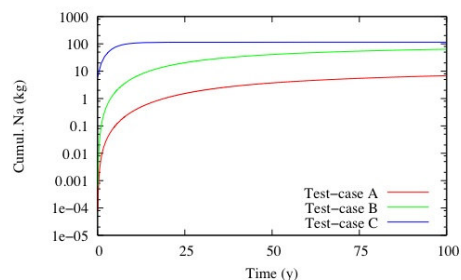


- Diffusion of alkaline (monolith → fractures) followed by slow advection
- Portlandite buffering vs CO_2 reactivity (→ calcite precipitation)

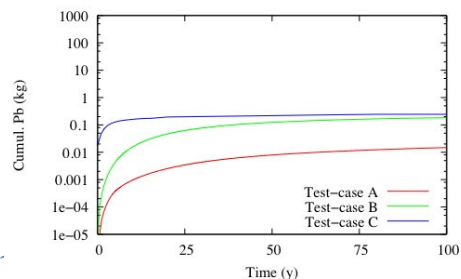


- Same diffusion-convection scheme
- Coupled to pH changes
- Pb may co-precipitate with calcite

Sodium and lead cumulative releases (100 y)



- Tracer, therefore relevant to assess the effect of hydrodynamic regime on release
- → clear contrasted behaviors



- Sensitive to both hydrodynamics and pH evolution
- However, the released lead fraction << dynamics leaching test ones

Concluding remarks

- Modelling the initial state required preliminary mineralogical analyses and batch leaching tests.
- This core source term model → dynamic leaching “3D” simulations considering, simultaneously, pore water evolution, mineralogical alteration fronts, and the concomitant release of elements.
- However, this is time consuming and the S/S waste evolution was not fully addressed due to the complexity of cement-based materials (especially for pollutants).
- Capability of reactive transport codes to extrapolate the laboratory results to a in situ scenarios, illustrated here by an hypothetical but demonstrative effect of cracking processes on long-term pollutant releases in landfills.
- Major perspective = unsaturated carbonation effect.

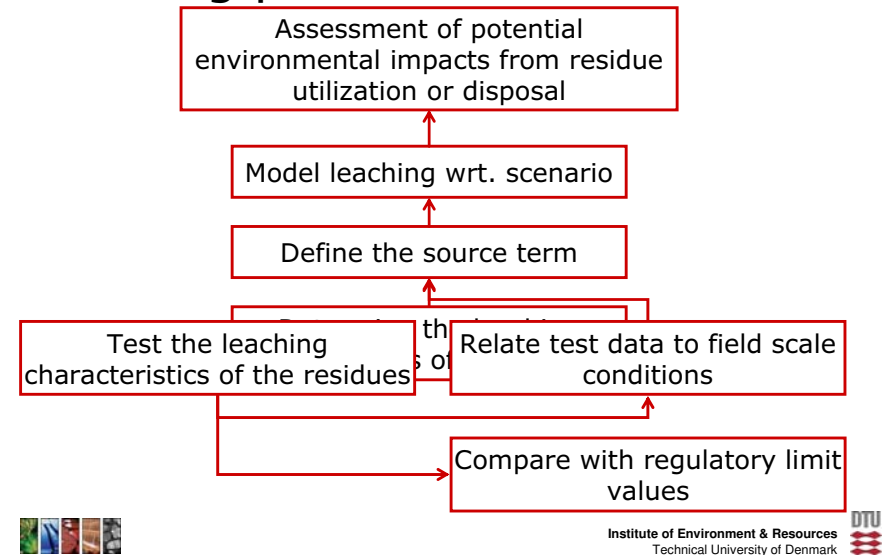
Predicting Cr leaching from waste incineration ashes

Thomas Astrup

Institute of Environment & Resources
Technical University of Denmark



Leaching prediction



Problems with Cr...

- Highly varying leaching data!
- Toxic element, present in two redox states: Cr(III) and Cr(VI)
- Critical element with respect to limit values for reuse of incineration residues
- Stabilization/pretreatment of residues often leads to increasing Cr leaching
- Difficulties with predicting Cr leaching based on common leaching tests

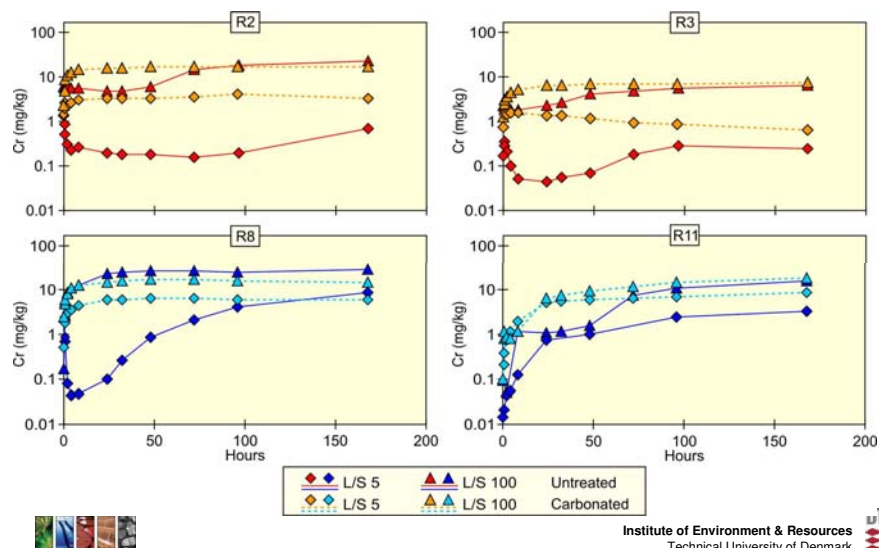


Purpose

- To explain variations in Cr leaching as observed in typical batch leaching experiments:
 - 11 APC residue samples from 8 different plants using dry, semidry or wet flue gas cleaning
 - batch experiments at L/S 5 and L/S 100
 - carbonated and non-carbonated samples
 - equilibration over 1 week
 - sampling over time
 - headspace in bottles was minimized



Cr release

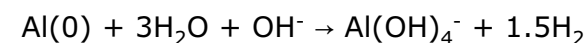
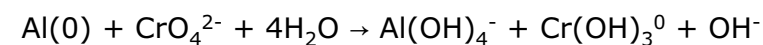
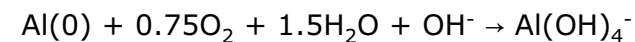


Cr release control

Solid phase dissolution:



Al(0) oxidation:



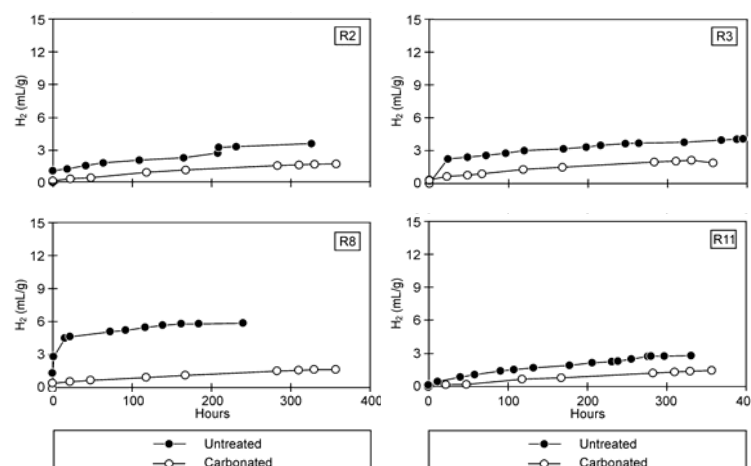
Reactivity of Al is important
The O_2 level is important



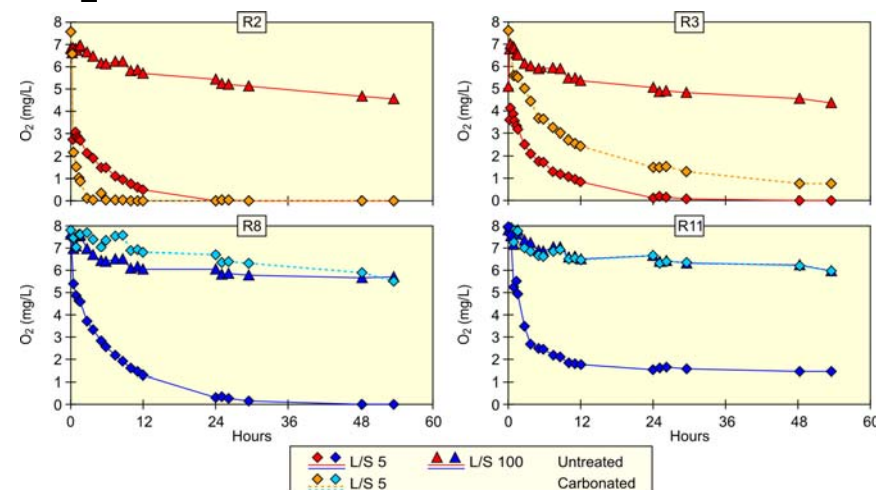
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Al(0) reactivity



O_2 depletion



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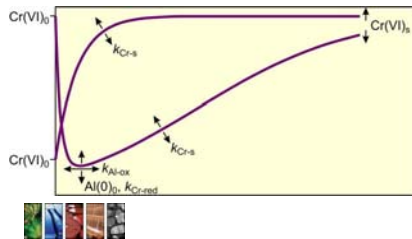
Cr release model

Al(0) oxidation by O₂, H₂O, Cr(VI):

$$\frac{d[\text{Al(0)}_r]}{dt} = -k_{\text{Al-ox}} [\text{Al(0)}_r]$$

Cr(VI) dissolution + reduction by Al(0):

$$\frac{d[\text{Cr(VI)}]}{dt} = k_{\text{Cr-s}} ([\text{Cr(VI)}_s] - [\text{Cr(VI)}]) - k_{\text{Cr-red}} [\text{Cr(VI)}] \cdot [\text{Al(0)}_r]$$

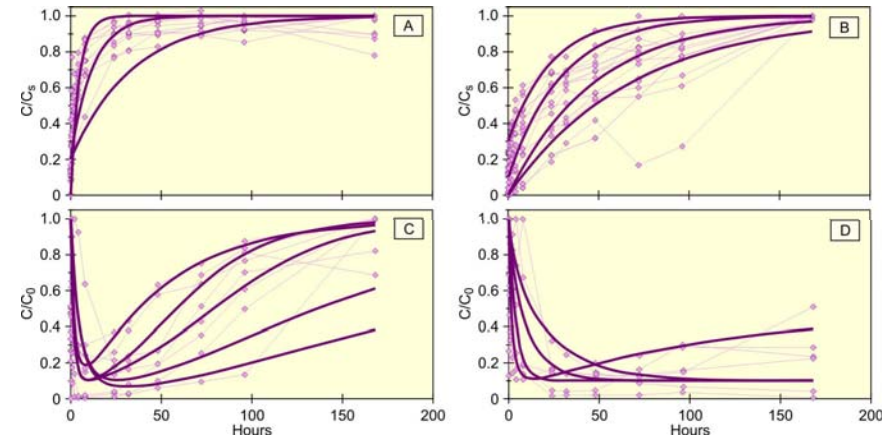


Model parameters				
	A	B	C	D
Al(0) ₀			250	250
				[mol]
k _{Al-ox}			1-5	5
				[h ⁻¹]
Cr(VI) ₀	0-0.2	0-0.3	1	1
				[mol/L]
Cr(VI) _s	1	1	1	0.1-0.5
				[mol/L]
k _{Cr-red}	0	0	0.02-0.05	0.005-0.05
				[mol ⁻¹ ·h ⁻¹]
k _{Cr-s}	0.7-5	0.35-1	0.1-1	0.2-5
				[h ⁻¹]

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Cr release model



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Al-O₂-Cr interactions

The available Al(0) reduction capacity relative to the O₂ level in the test system is important for the resulting Cr concentration:

- Al(0) reactivity
- L/S ratio of the test (O₂ level)
- Headspace volume
- Mixing/agitation

Sample handling / pretreatment is also very important!

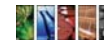


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Example: sample handling

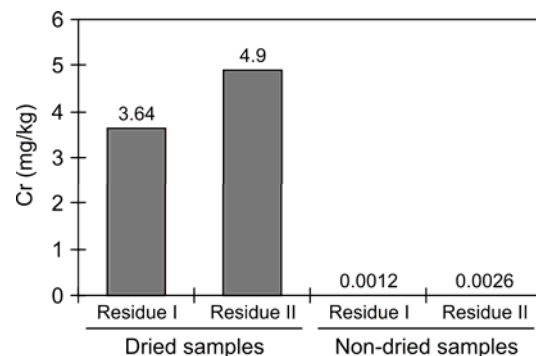
- CEN batch test at L/S 2
- Two pretreated APC residues
(Ferrox: washing + FeSO₄ addition + oxidation of Fe-oxides)
- Samples were tested dried as well as non-dried
(accounting for the water content)



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Example: sample handling



Conclusion

Bad news:

- Cr leaching data from typical batch leaching tests may not be trusted for assessment purposes...
- Cr leaching is strongly affected of Al-O₂-Cr interactions in the test system
- Cr leaching depends on parameters like sample handling, headspace volume, L/S ratio, mixing

"Good" news:

- You may easily "design" the Cr concentration level in the test...

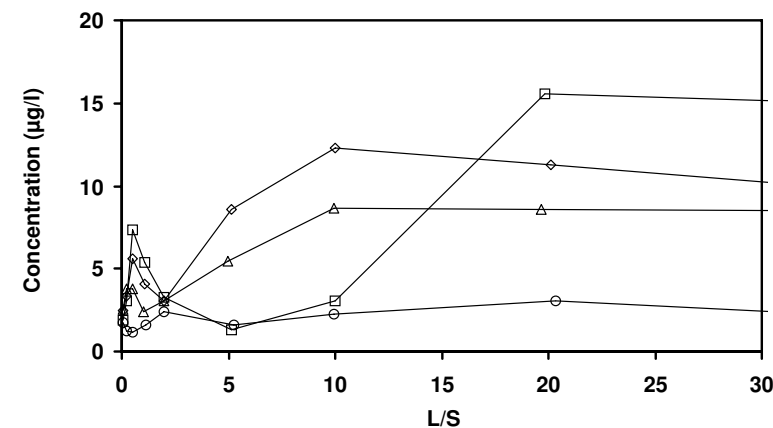


Thank you

Astrup, T.; Rosenblad, C.; Trapp, S.; Christensen, T.H. (2006): Chromium release from waste incineration air-pollution-control residues. *Environ. Sci. Technol.*, 39, 3321-3329.



Example: column experiments

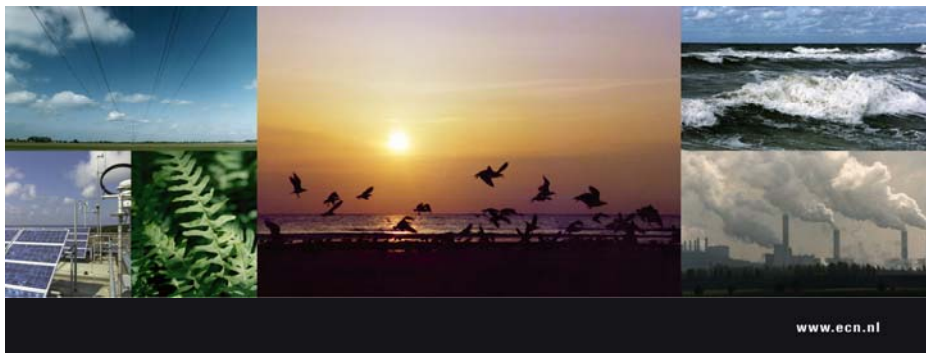


Cr leaching from 4 different bottom ashes



Predicting Leaching of Reactive Substances from Porous Monolithic Materials with Orchestra-LeachXS

Hans Meeussen and Hans van der Sloot



www.ecn.nl

Predicting Leaching of Reactive Substances from Porous Monolithic Materials with Orchestra-LeachXS

Outline

- ✓ Introduction
- ✓ Model structure
- ✓ Results
- ✓ Conclusions



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Introduction

- The leaching behaviour of cement based porous materials determines their environmental impacts
- To assess leaching behaviour short term (tank) leaching tests have been used to fit empirical diffusion models
- **Advantage:** simple modeling, no understanding of system required.
- **Disadvantage:** impossible to estimate sensitivity of system to (changing) conditions (e.g. changes in pH as a result of carbonation or other leachant).

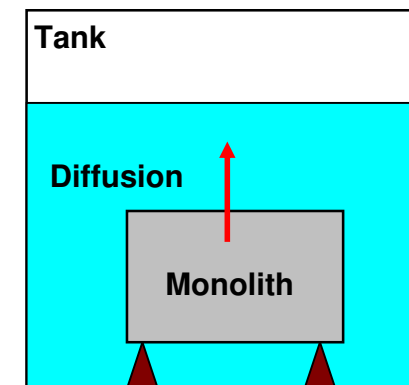
Aim of this work:

- To model leaching behaviour of cement based products in a mechanistic way.
(use advanced chemical speciation model to calculate effective diffusion coefficients)
- Predict leaching behaviour from independent parameters.
- Use tank leaching tests to validate how well this works.
- Extrapolate to predict leaching behaviour under application scenario conditions.

Experimental System: Monolithic Tank Leaching Test

Sample of monolithic material placed in tank with a leachant (usually demineralised water)

Concentrations of leaching substances measured after different leachant renewal times

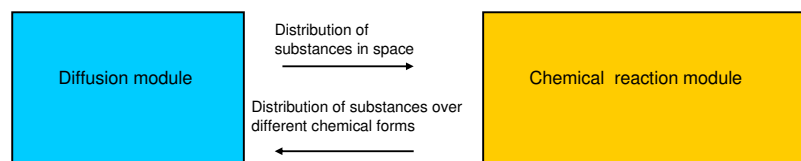


Numerical Model Components

Model components

- Molecular Diffusion Model, (Fick's law, 3d)
- Chemical reaction model

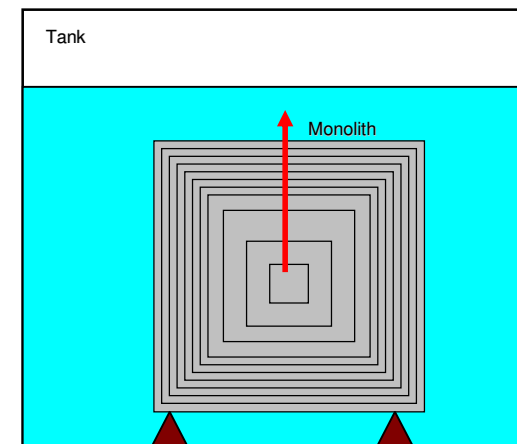
(multi-component chemistry, aqueous speciation, precipitation dissolution, surface complexation, adsorption, solid solutions, activity corrections)



Numerical Model Structure

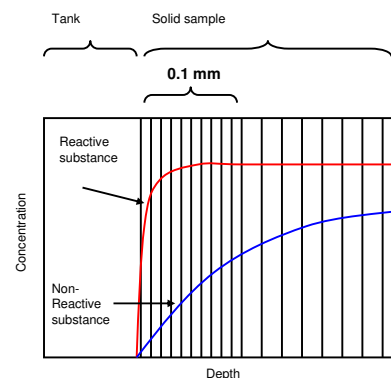
Molecular Diffusion Model (1d)

- Finite differences
- 20 cells
- Different volumes
- Different sizes
- Different contact areas
- Unevenly spaced
- Outer 5 cells 2 μm thick



Numerical Diffusion Model: Spatial discretization

- Challenge: Very steep concentration gradients for dissolving/precipitating substances
- pH, Ca, Al, SiO_4 , Mg,
- Requires fine grid, small cells (1-10 μm)
- Short time steps (seconds)
- Very computing intensive (hours)
- 64 day case = ca. 20.000.000 equilibrium calculations
- ORCHESTRA efficiently uses 4 processors



Input Data for Orchestra/LeachXS Modelling

Chemical Parameters

Physical Parameters

Refresh Parameters

Model Output:

pH dependence test

- Predicted dissolved concentrations versus measurement
- Partitioning of elements between dissolved and particulate phases

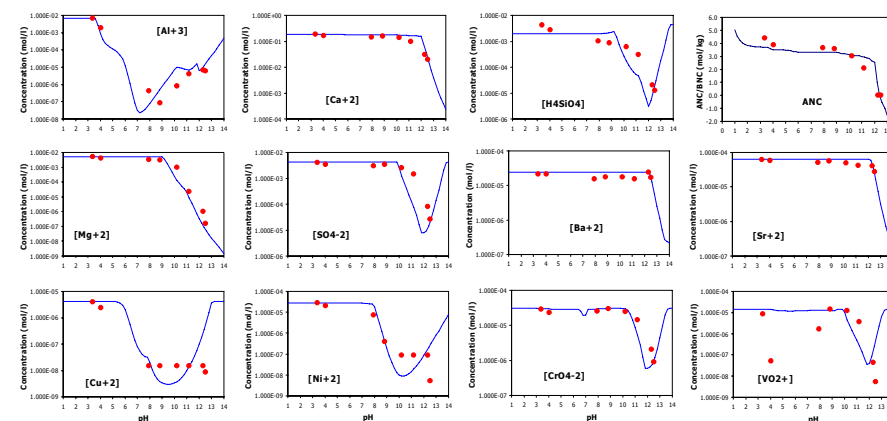
Dynamic monolith leach test

- Concentration profiles of substances in sample as a function of time and as a function of depth
- Dissolved concentrations in the tank as a function of time

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Results of Orchestra/LeachXS Prediction for cement mortar

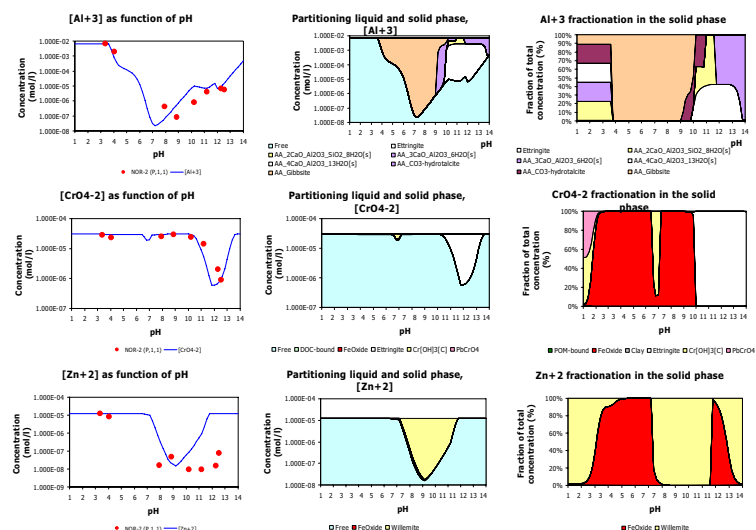


Simultaneous modelling of > 25 elements with all relevant phases identified by SI run

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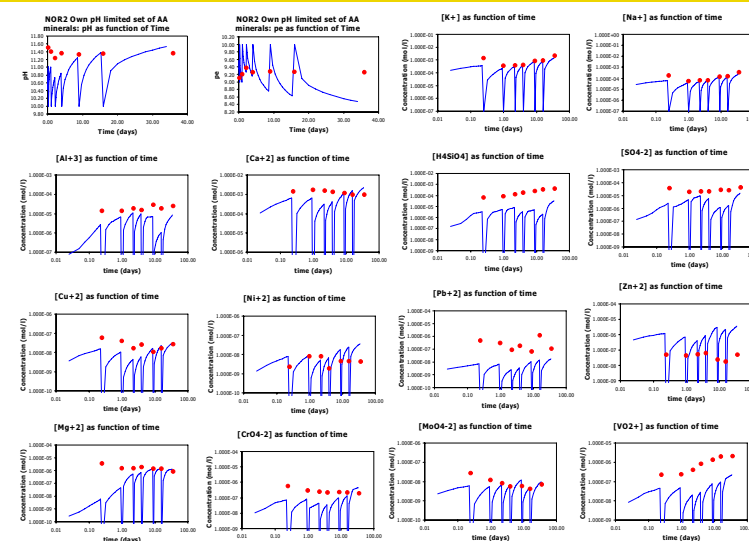
Partitioning of elements for cement mortar



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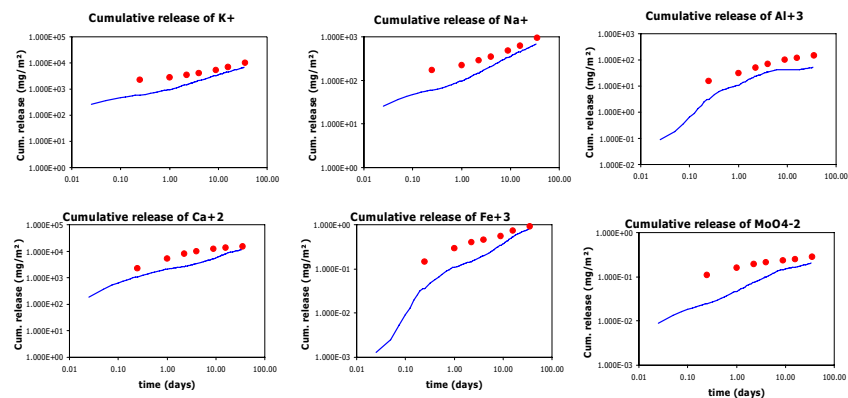
Prediction of DMLT with renewal



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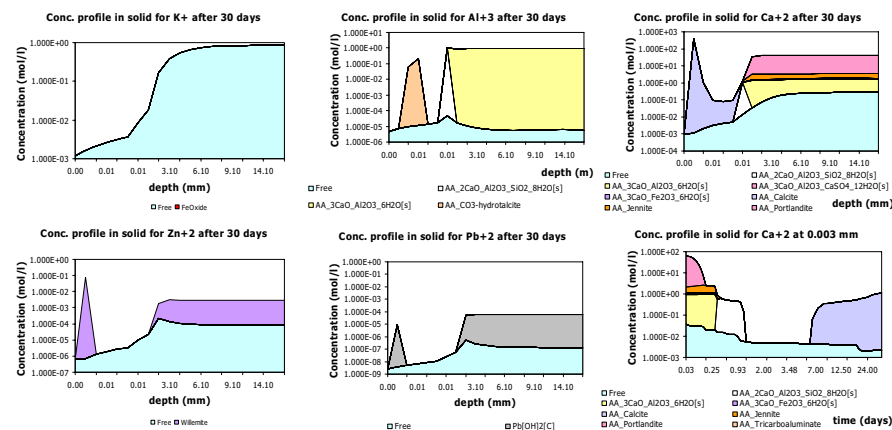
Cumulative release as predicted for cement mortar



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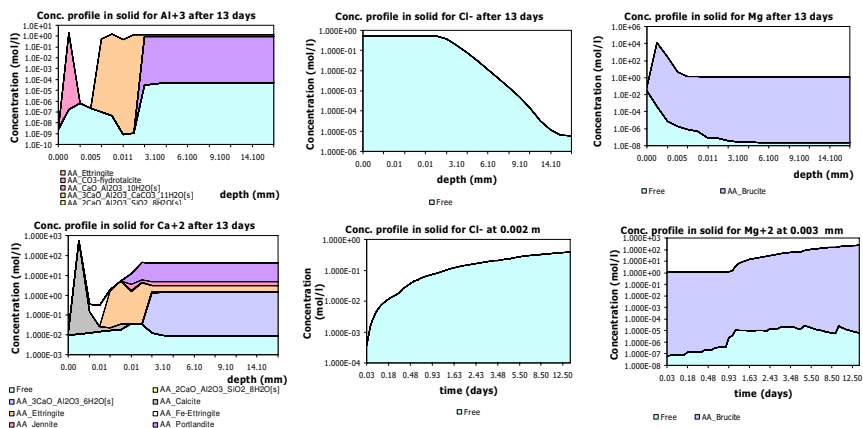
Predicted profile of cement mortar after carbonation



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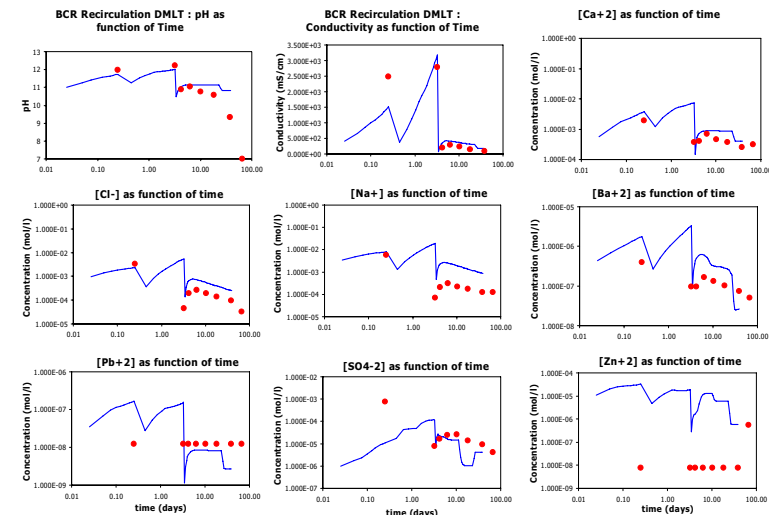
Predicted profile of cement mortar in contact with seawater



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15

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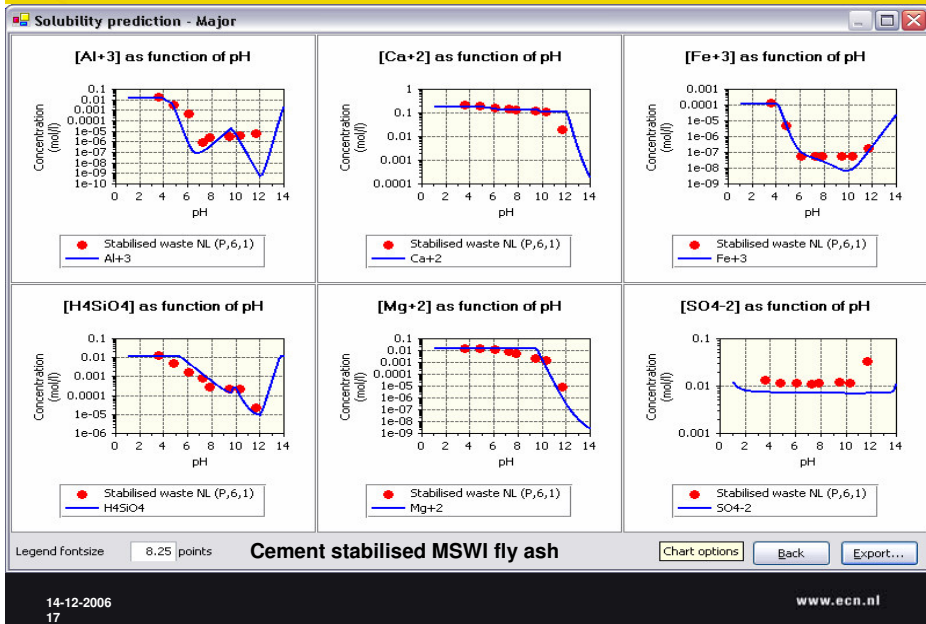
Prediction of DMLT with continuous flow (BCR mortar WG6)



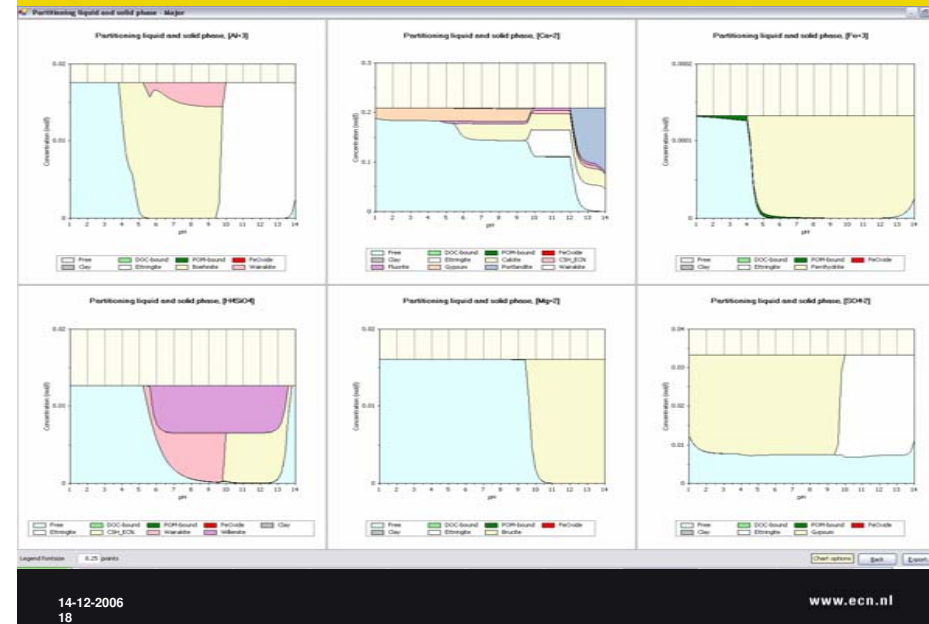
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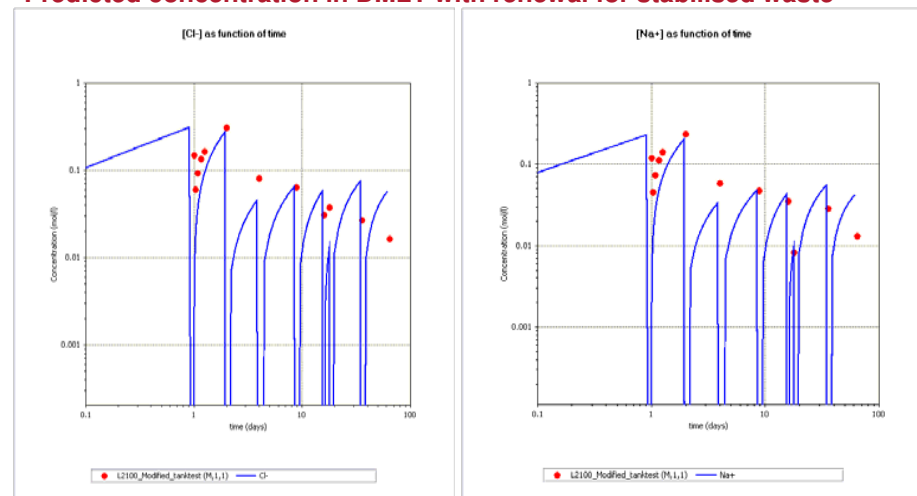
ECN Predicted concentration for stabilised waste (pH stat)



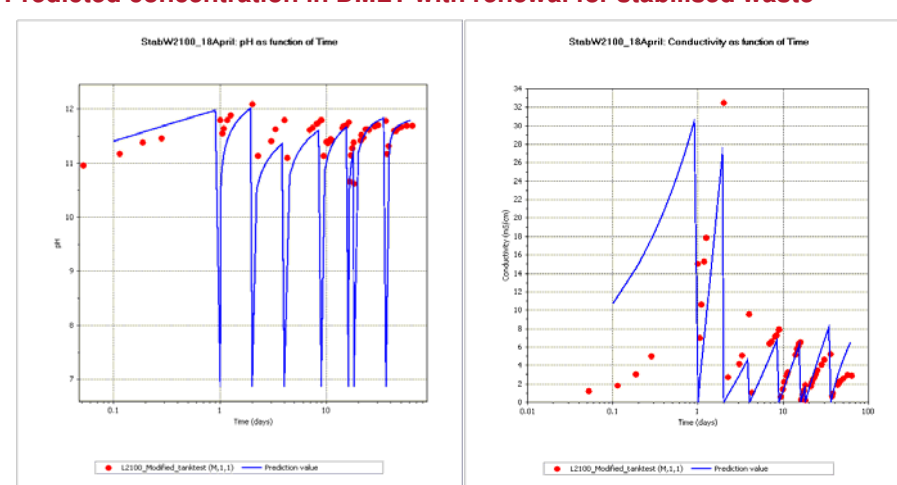
ECN Partitioning of elements for stabilised waste (pH stat)



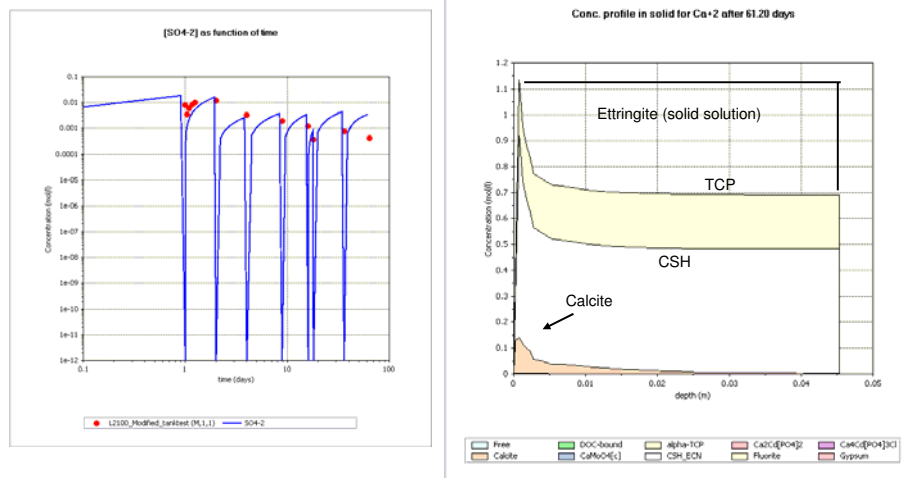
Predicted concentration in DMLT with renewal for stabilised waste



Predicted concentration in DMLT with renewal for stabilised waste



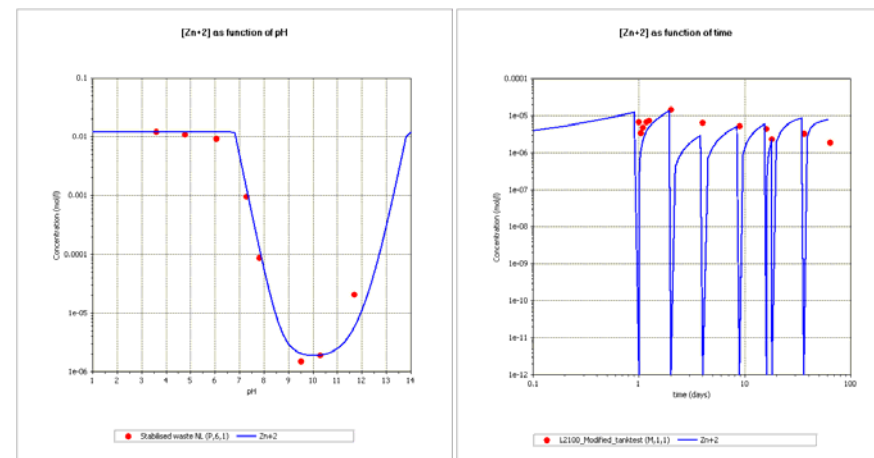
Predicted concentration in DMLT with renewal for stabilised waste



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21

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Predicted concentration in DMLT with renewal for stabilised waste

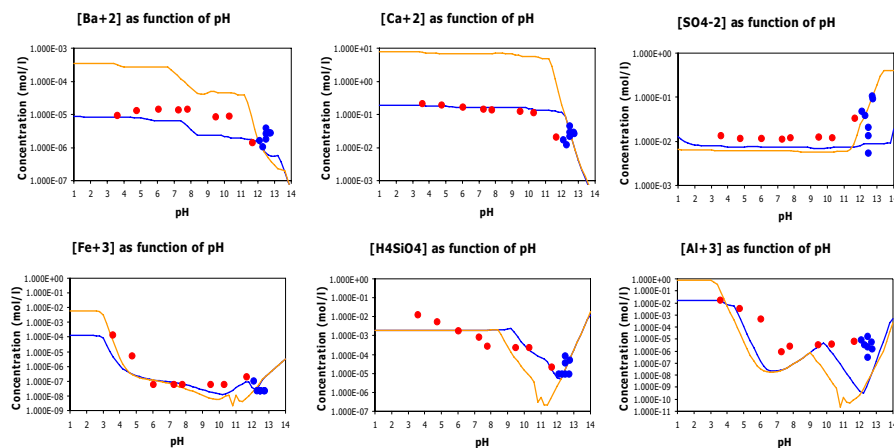


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22

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Cement Stabilised Waste (MSWI fly ash)

Percolation test data in relation to pH dependence test data

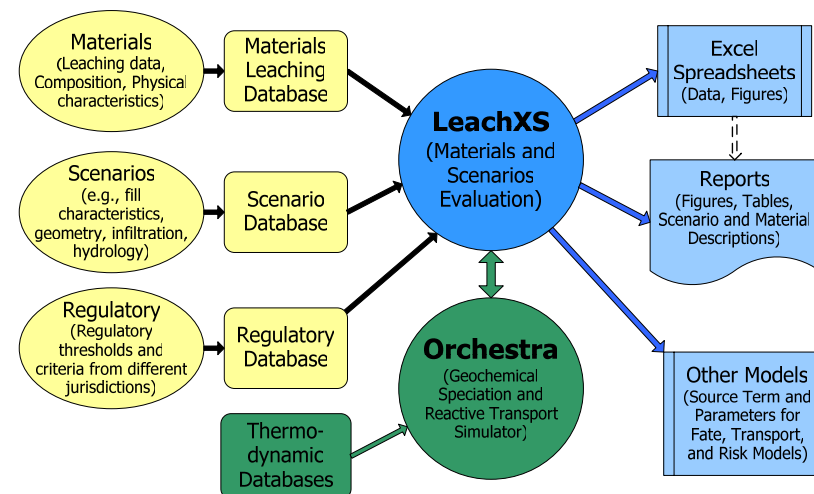


Simultaneously modelling release as a function of pH and release at low L/S (TS14405) to capture relevant mineral phases at porewater conditions

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LeachXS Structure



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Conclusions

- Modelling of leaching behaviour of wide range of substances from cement based products in a mechanistic way starts to become possible.
- Mechanistic model will describe tank test less accurately than empirical model fitted on this test
- However, increased insight into processes that control leaching behaviour enable extrapolation to different (environmental) conditions and longer timescales.
- This particularly relates to the partitioning in the pores as a function of depth into the specimen. This is relevant for other exposure environments (e.g. seawater)
- By full element evaluation important interaction can not be missed (e.g. Pb is influenced by oxyanions Mo, V, Cr)
- Experimental validation of mechanistic model under different conditions required
- First fraction of column test very suitable condition to assess porewater conditions to identify minerals that are depleted at L/S=10 batch

Leaching of contaminants from MSWI bottom ash used as subbase in road construction: Results from a pilot scale test site

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DHI – Water & Environment

Agern Allé 5

2970 Hørsholm, Denmark

Funded by DAFONET, Denmark

BRGM Workshop

Source Term: from characterisation to prediction
Paris, October 19 - 20, 2006

Test site for utilisation of MSWI BA

Test site for use of MSWI bottom ash as
sub-base in roads and squares/parking
sites

October 2002 – October 2005

Justification:
Danish Statutory Order 655 of 27 June
2000

Main objectives:

- To describe the contamination source term and its dependency of i. a. time, cover, BA type
- To evaluate the preconditions and possibly suggest improvements of the risk assessment upon which the Statutory Order is based



Characterisation in the laboratory
(composition, column, batch, pH-
static leaching tests)

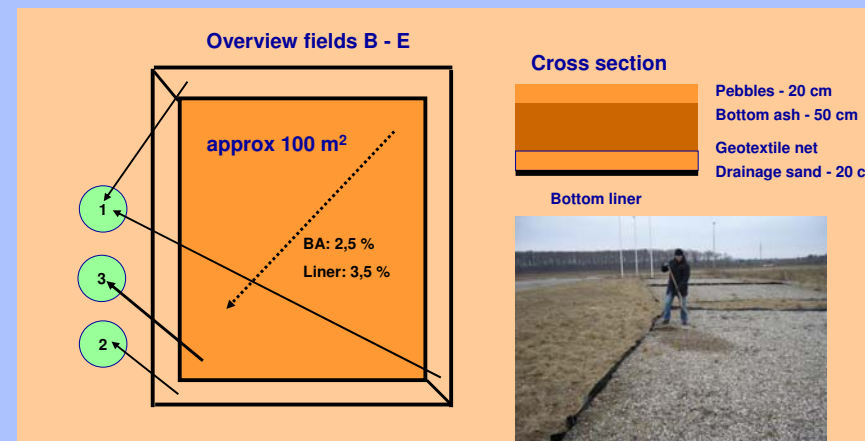
Field observations (quantity and
quality of leachate as a function of
time and L/S)

Scenario calculations using the data

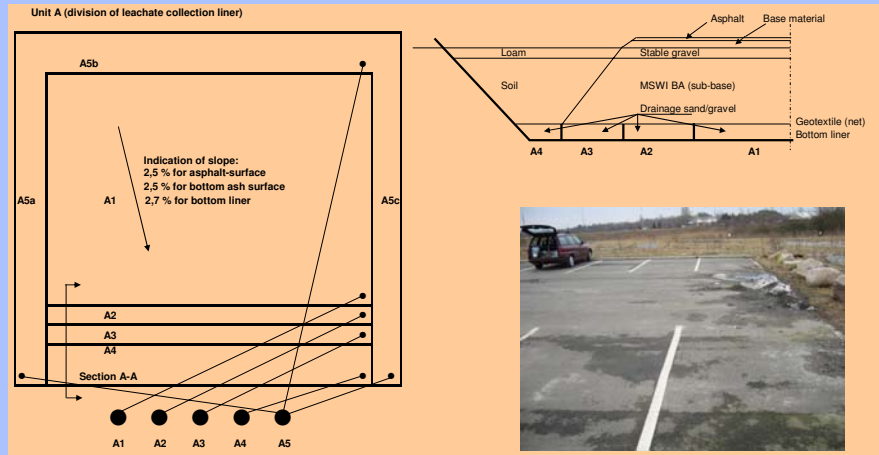
Test fields

Field	BA type	Major objective to study:	Top cover	Bottom liner
A	MSWI 1	Infiltration rate	Asphalt	LDPE
B	MSWI 1	Infiltration rate	Flagstones	LDPE
C	MSWI 1	Leachate quality	Pebbles	LDPE
D	MSWI 2	Leachate quality	Pebbles	LDPE
E	MSWI 3	Leachate quality	Pebbles	LDPE

Description of fields B - E



Description of field A

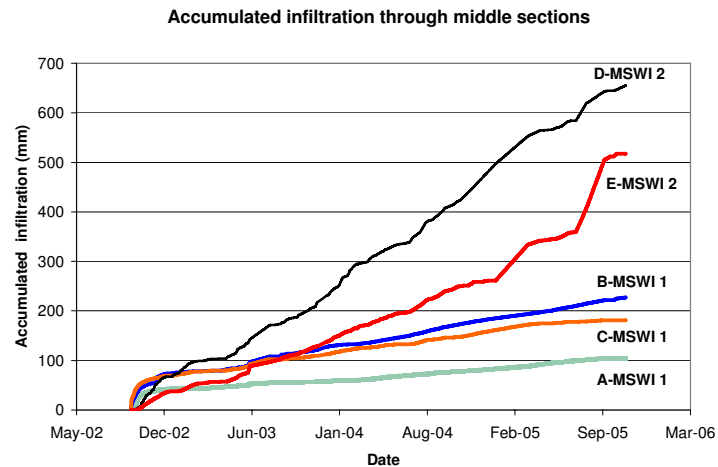


Leachate collection wells



Leachate production rates – middle sections

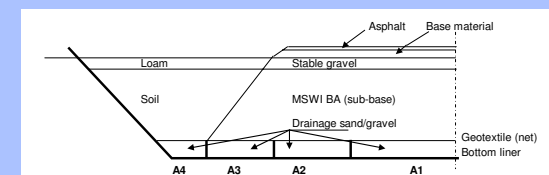
Total precipitation: 2000 mm



Leachate production – field A

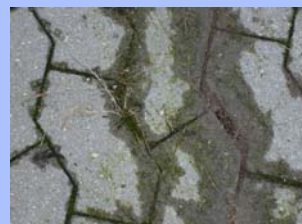
October 2002 – October 2005

Section of bottom liner	Part of surface	Part of leachate	Part of accum. precipitation	Accum. L/S Oct. 05
	%	%	%	l/kg
A1 – Middle section	52	3.7	3	0.11
A2 – Edge under asphalt (BA)	4.2	2.5	2	0.89
A3 – Edge downstream of asphalt (BA + soil)	4	2	1.6	1.4
A4 – Edge downstream of asphalt (soil)	8.6	57	46	-
A5 – Other 3 edge sections	31	35	29	3
A – All sections	100	100	82	2



Leachate production – field B October 2002 – October 2005

Section of bottom liner	Part of surface %	Part of leachate %	Part of precip. %	Acc. L/S Oct. 2005 l/kg
B1 - upstream edges	17	22	16	2,2
B2 - downstream edges	21	69	50	5,5
B3 – middle section	62	9,4	6,8	0,23
B - all sections	100	100	73	1,6



Leachate production – site C, D and E October 2002 – October 2005

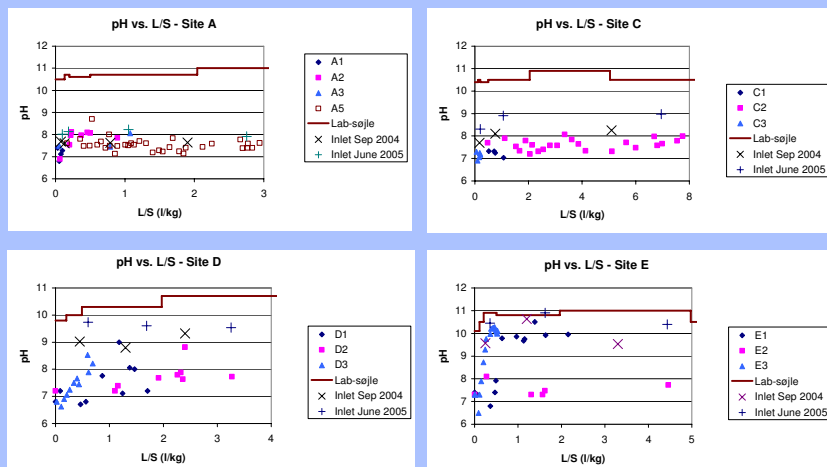
Test unit	Origin of BA	Top cover	Percentage of precipitation collected as leachate				L/S for middle section (l/kg)
			Upstream edges	Downstream edges	Middle section	Total	
C	MSWI 1	Pebbles	11.1	57.2	5.7	74	0.20
D	MWSI 2	Pebbles	17	30.9	17.2	65.2	0.69
E	MSWI 3	Pebbles	16.6	41	9.4	66.9	0.52
Approximate percentage of area			17 - 24	21 - 23	55 - 62	100	

Surface runoff to infiltration ratio over a distance of 8 m:

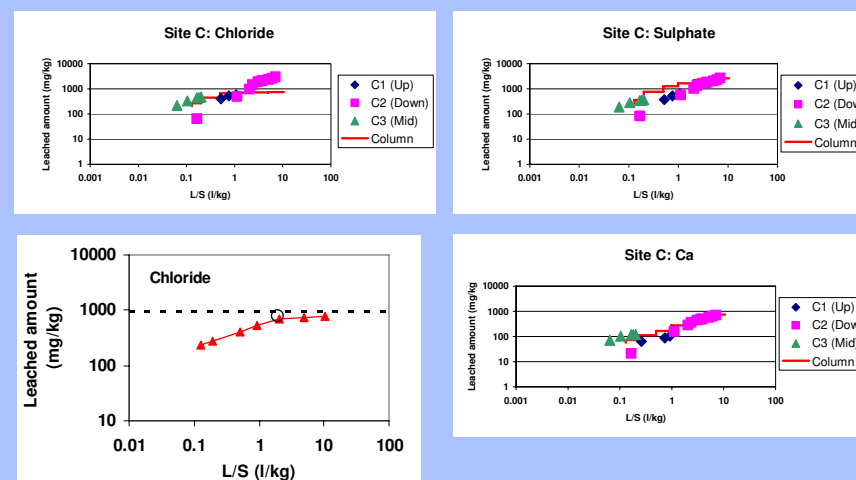
C: 7:1

E: 2:1

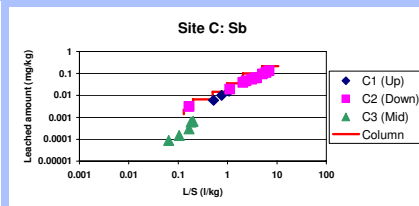
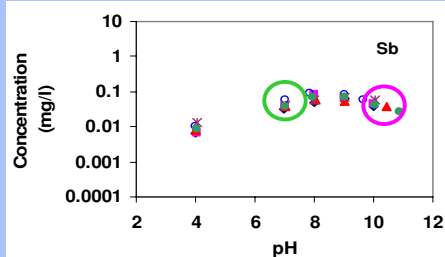
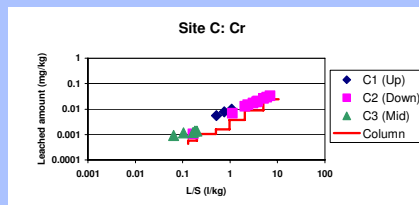
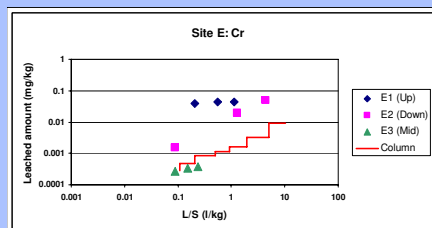
Leachate quality – Field vs. lab pH as a function of L/S



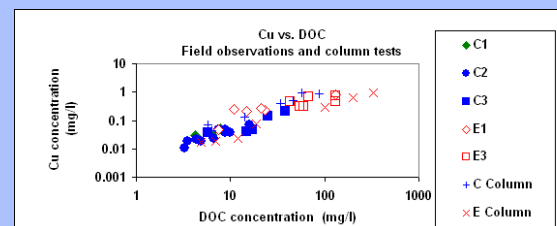
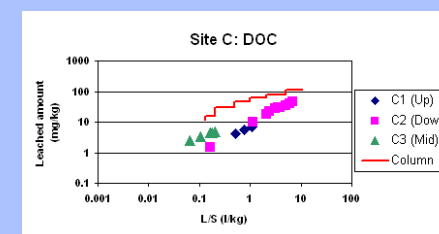
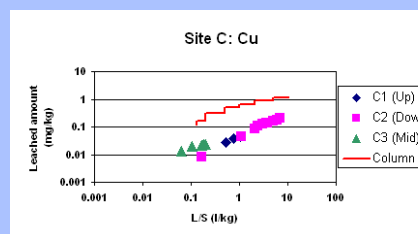
Leachate quality – Field vs. lab Leached amounts of salts vs. L/S



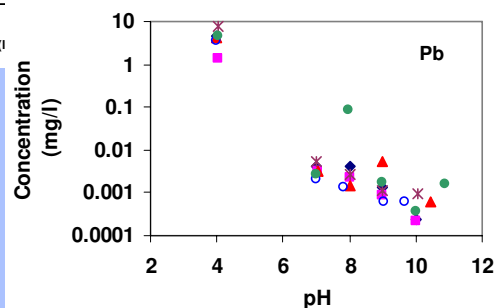
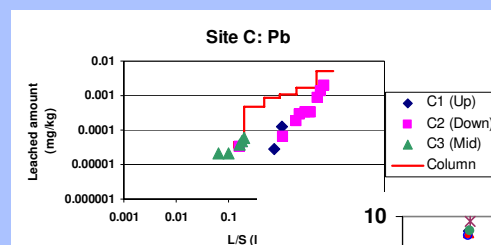
Leachate quality – Field vs. lab Leached amounts of trace elements vs. L/S



Leachate quality – Field vs. lab Cu and DOC as a function of L/S



Leachate quality – Field vs. lab Trace elements as a function of L/S



MSWI BA quality in relation to Statutory Order 655 of 27 June 2000

Based on lab characterisation, the leaching criteria for utilisation as "category 2" are exceeded for **chloride**, **sulphate**, **Na**, **Cu** and (in 2 cases) **Cr**

Temporarily increased leaching criteria for category 2 for chloride, sulphate and Na are met.

Criteria for utilisation as "category 3" (under more restrictive conditions than "category 2") are met.

Source strength of selected components over a 3-year period

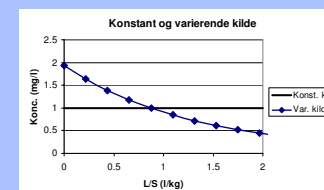
Total amounts leached during 3 years						
Component	Unit	Site A	Site B	Site C	Site D	Site E
Top cover	-	Asphalt	Flagstones	Pebbles	Pebbles	Pebbles
Type of BA	-	MSWI 1	MSWI 1	MSWI 1	MSWI 2	MSWI 3
Total infiltration	mm	1650	1500	1500	1450	1650
Chloride	kg/m ²	0.41	0.63	0.80	0.73	1.8
Sulphate	kg/m ²	0.24	0.39	0.72	0.45	0.70
Cr	g/m ²	2.1	8.5	7.5	13	23
Cu	g/m ²	26	59	53	11	180

De-icing of roads: 0.6 to 2 kg/m² of chloride per year

Evaluation of conditions used in Statutory Order 655 of 27 June 2000

Constant/variable source with and without sorption

Component	K (kg/l)	DHI model Limit values in mg/kg for L/S = 2 l/kg		
		Constant source No sorption	Variable source sorption	No Variable source Sorption included
Chloride	0.75 (0.57)	4600	1300	1300
Sulphate	2.0 (0.33)	5800	3200	3200
Cr (total)	0.18 (0.18)	0.82	0.7	1.4
Cu	1.0 (0.28)	3.6	1.6	42



Conclusions

- Different types of MSWI BA may produce different amounts of leachate and different fluxes of several contaminants when used as sub-base under the same conditions.
- The flow pattern plays an important role for the source term. Considerable amounts of precipitation may flow laterally on (or in) sloped surfaces of compacted BA. Dual flow regimes are likely to occur.
- Substantial differences in pH have been observed in field leachate and leachate from laboratory column tests, probably due to preferential flow, processes in the BA and CO₂ uptake in the system.
- Fairly good agreement between lab and field results was seen for most salts and many trace elements (middle sections), but e.g. not for Cu og DOC (and in some cases Pb). DOC will change with time, and strongly affect Cu (and others). Differences for Cr from the edge sections may be explained by oxidation.

Conclusions (2)

- An asphalt cover will substantially reduce the leachate production rate and the rate of release of contaminants from the BA sub-base. Flagstones appear not to do so.
- Model environmental impact calculations using data from the study indicate that the use of a varying source strength and sorption (LFD concept) will only produce less stringent criteria than a model based on constant source strength without sorption for contaminants with relatively fast release (high kappa) and substantial sorption.

Workshop Source Term From characterization to Prediction

October 19-20, 2006

Pilot scale data input
in understanding and prediction of leaching behaviour
of utilisation of waste in civil engineering



POLDEN / Jacques Méhu & Gwénaëlle Bröns-Laot

1

Pilot scale data input in understanding and prediction of leaching behavior of utilization of waste in civil engineering

- 1 - Application of EN 12 920 : Analysis of European implementation cases (BILENV)
- 2 – Considered waste / scenarios combinations
- 3 – Fields of improvement
- 4 – Case study : stabilized MSWI fly ash used in road applications



POLDEN / Jacques Méhu & Gwénaëlle Bröns-Laot

2

BILENV 10 Programmes taken into account

- (1) **BRITE EURAM METALEUROP** : Valorization of Pb-Zn primary smelters slags, METALEUROP (for the European Commission) 1997 (POLDEN & ECN)
- (2) **CAEN** : Underground quarry backfilling with MSWI bottom ash-containing mortars :. INERTEC 2003
- (3) **LANDFILL DIRECTIVE** : “Acceptation of inert wastes, annexe 2 of Directive 1999/31/CE, concerning landfilling of wastes”, TAC working group : France (BRGM, INSA de Lyon, Ministère de l’Environnement) ; The Netherlands (ECN, VROM) ; UK (WRC, Ministry of Environment) ; Germany (Ministry of Environment - BMU) ; Danmark (DHI, Ministry of Environment) ; Autriche (Ministry of Environment) ; Suède (SGI) .



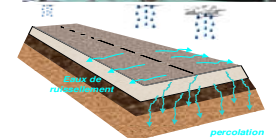
3

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3

BILENV 10 Programmes taken into account

- 4) **ECOCOMP** : Research programme on ecocompatibility of waste, POLDEN - ADEME 1999
- 5) **GHOST** : Research programme on ecocompatibility of a heap of salted wastes from the soda industry, POLDEN SOLVAY ADEME
- 6) **REVASOL** : Utilisation of treated fly ash from MSWI issued from NEUTREC process, POLDEN - BERTIN – SOLVAY-ADEME en 2003
- 7) **SNET- EDF** : Assessment of Environmental Impact of utilisation of silico-alumineus coal fly ash in road application, POLDEN - EDF-SNET in 2000



4

POLDEN / Jacques Méhu & Gwénaëlle Bröns-Laot

4

10 Programmes taken into account

- (8) **SVDU** : *Environmental impact assessment of the use of municipal solid waste incineration bottom ash in roadwork*, CREED-LCPC-BRGM-SVDU-ITASCA) –ADEME
- (9) **VALOMAT** : *New civil engineering materials based on bottom ash valorisation*, SOLETANCHE-BACHY – POLDEN (for the European Commission) in 2001
- (10) **VIVALDI** : *Programme "VIVALDI" on vitrified fly ash from MSWI Bordeaux Métropole : Annexe 1 : Assessment of long term leaching behaviour* EUROPLASMA - ADEME - CEA in 2000



Considered Combinations

			Soda production residues	Coal Fly ash	MSWI Fly ash	Demolition wastes	MSWI Bottom ash	MSWI APC residue	Zinc 1st smelting slag	Lead 2nd smelting slag	vitrified APC residue
Building	Foundation	concrete	←	←	←	←	←	←	BRITE EURAM		
Building	Outdoor wall	concrete	←	←	←	←	←	←	BRITE EURAM		
Building	Outdoor wall	Sand lime brick	←	←	←	←	←	←	BRITE EURAM		
Building	Outdoor wall	block	←	←	←	←	←	←	BRITE EURAM		
Storage	Waste landfill	Waste as it stands				DIRECTIVE					VIVALDI
Storage	Heap	Waste as it stands	GHOST							ECOCOMP	
Civil Engineering	Water reservoir	mortar					↓	ECOCOMP			
Civil Engineering	Quarry backfilling	mortar					VALOMAT				
Civil Engineering	Quarry backfilling	mortar					CAEN				
Civil Engineering	Road base layer	Bitumen concrete	←	←	←	←	←	←	BRITE EURAM		
Civil Engineering	Road base layer	Gravel concrete	←	←	←	←	←	←	BRITE EURAM		
Civil Engineering	Road foundation layer	Waste as it stands					SVDU				
Civil Engineering	Cast concrete wall	concrete	←	←	←	←	VALOMAT				
Civil Engineering	Open backfill	Waste as it stands	←	←	←	←	ECOCOMP		BRITE EURAM		

Benefits of the application of ENV12920

- **Better awareness of the notion of scenarios by the stakeholders**
 - ✓ Understanding that compliance cannot replace characterization (still a problem for some people in some regulatory bodies)
 - ✓ Understanding that field LS ratio are far below lab LS and that concentrations and pH can be much higher !
 - ✓ Understanding of the interest of ecotoxicity as a complementary approach of emission assessment
 - ✓ Understanding that reference material and not systematically "pure nor safe" material !
 - ✓ Understanding that modeling is not systematically a theoretical mathematical practice but can (should be) explicit and transparent (still a problem sometimes)



Benefits of the application of ENV12920

Better understanding of behaviour controlling factors

- ✓ Nature of factors (special hydrodynamics of a heap)
- ✓ Hierarchy between factors (pH > LS)
- ✓ Values (e.g. infiltration higher than expected)

Allowing decision making on a clear basis

- ✓ Emission of pollutants can be predicted on the basis on a consensus for exposure conditions and time scale
- ✓ Relation with downstream environmental quality criteria can be established (Landfill Directive)
- ✓ Waste which could have been recycled based on the compliance test turned to be dangerous and non recyclable due to behaviour at real pH
- ✓ By the contrary industrial operations integrating waste materials in civil engineering have been realized thanks to the EN 12920 implementation and results



Main fields of improvement

1. Description of the scenario

- ✓ Confusion between data from the industrial reality (extreme complexity) and the significative data to be considered (conceptual scenario)
- ✓ Exposure conditions not always specified

2. Selection of the tests

- ✓ Not always links between identified influence factors at previous step and the performed tests
- ✓ Non justified tests or without any exploitation of the results
- ✓ identified influence factors without any associated tests



Main fields of improvement

3. Modeling

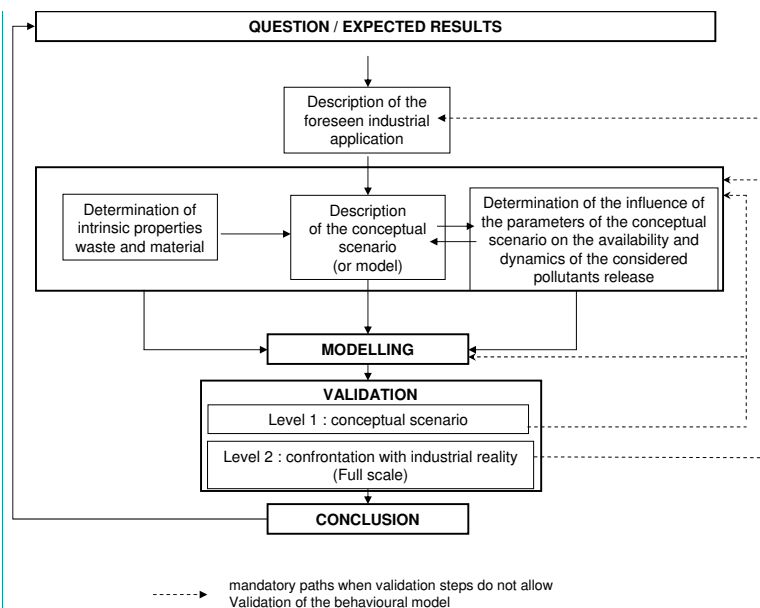
- ✓ Mentioned factors and/or measured data non integrated in the predictive mathematic modeling
- ✓ Decision or diagnosis based on a direct exploitation of the experimental data (pilot scale) without any calculation
- ✓ Selection of mathematical tools not always rational (i.e. based on the true nature of the phenomena to be considered) but often linked to the scientific background of the operators (mineralogy, chemistry, hydrodynamics, mass transfer,...)



Main fields of improvement

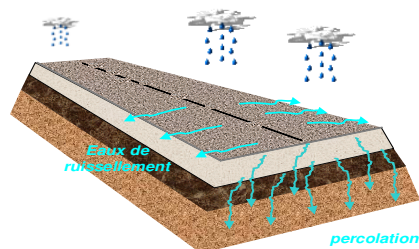
4. Validation

- ✓ Not always a validation step
- ✓ Pilots not always designed for this purpose
- ✓ Pilots with a non expected behaviour (not in the conceptual scenario (accidental spill))
- ✓ Results different from the prediction without resolution of the problem (like an adaptation of the model with integration of neglected factors in the conceptual scenario (carbonation, bio leaching,...))
- ✓ Problem of different scales of validation (pilots and instrumented full scale works) leading to different results without understanding.



Case study : Fillers elaborated from stabilized MSWI fly ash used in different types of road applications : Lab, pilot and full scales of experimentation

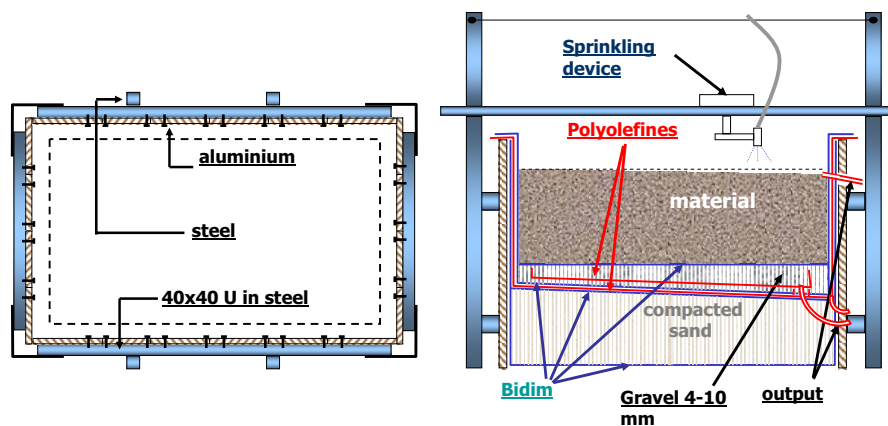
- Full application of the EN 12 920 standard
- Treated fly ash used as filler in hydraulic-binder-treated road base material (treated fly ash : 12 % and hydraulic binder : 3.5%)



Case study : Experimental program

- Laboratory batch static tests : intrinsic properties (Maximal available fractions, acid/base neutralisation capacity and solubilisation versus pH)
- Laboratory dynamic test : percolation test with hydrodynamic study
- Pilot test : one with waste-containing material and a reference one
- Field test : one with waste-containing material and a reference one

Case study : Pilot scale study

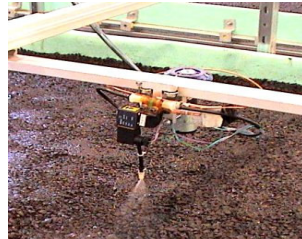


Case study : Pilot scale study

Setting by
EUROVIA of
the road
pilots on
EEDEMS



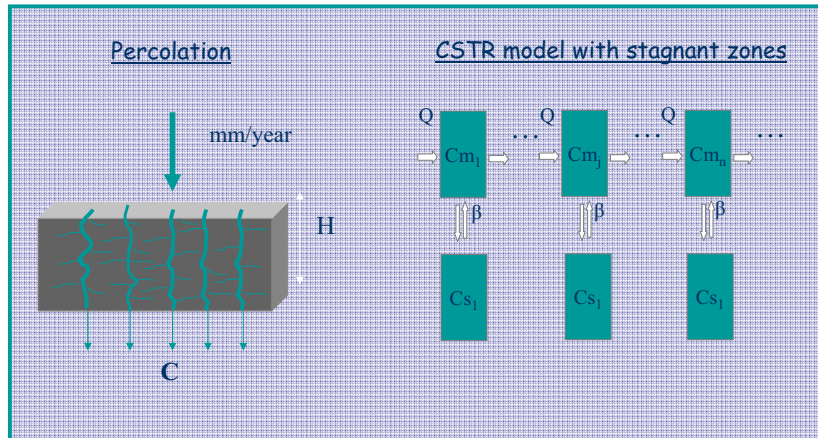
Case study : Pilot scale study



Case study : Pilot and Field Tests Follow-up

- Water balance
(water supply, rainfall, percolation or runoff)
- Physico-chemical follow-up of eluates
(pH, conductivity, major, salts, metals ...)
- Ecotoxicological follow-up
(Inhibition of the mobility of *Daphnia magna*, mortality and inhibition of the reproduction of *Ceriodaphnia dubia*)

Case study : Modeling

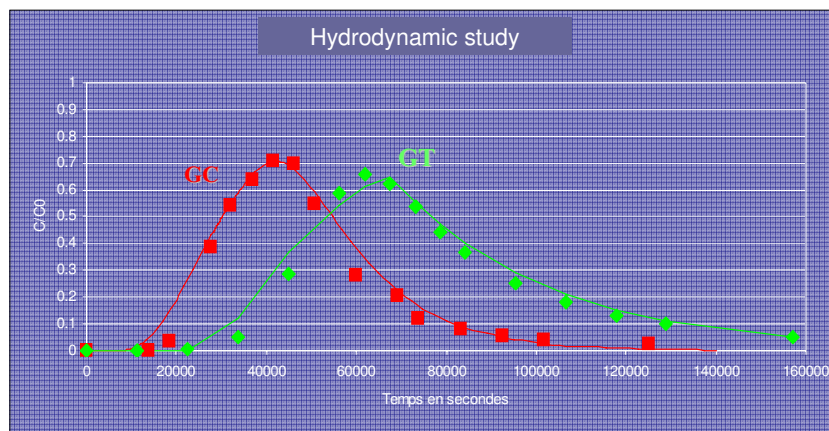


Case study : Modeling

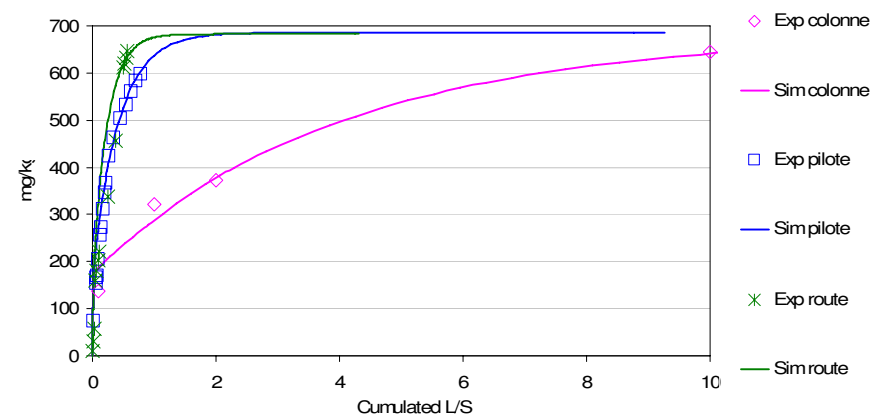
Mecanisms taken into account

- transport due to the circulation of water (hydrodynamics of the system) via 3 phenomena :
 - convection in the porosity
 - dispersion due to the heterogeneity of the material
 - gradients of concentrations and exchange between mobile zones (percolating porosity) and immobile («stagnant») zones
- chemical interactions (reactions of dissolution / precipitation)

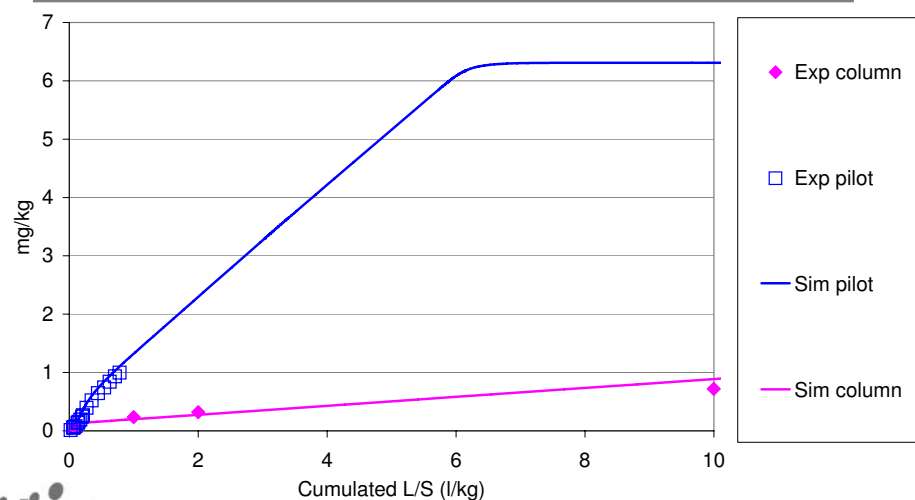
Case study : Results



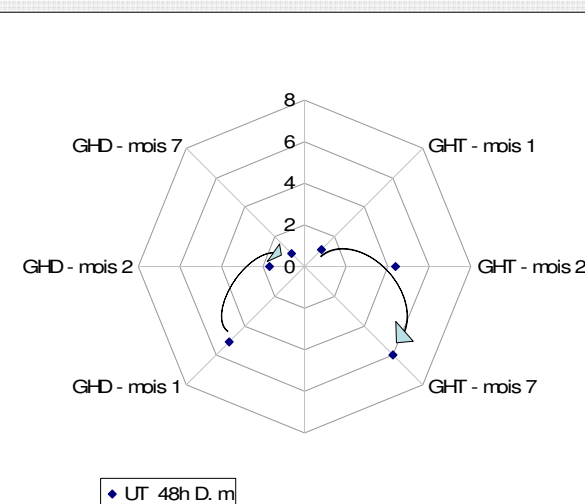
Case study : Results – Cumulated release of Cl^-



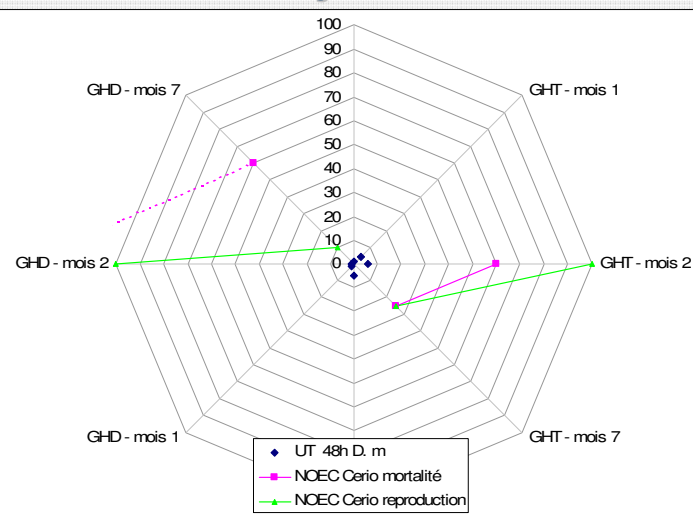
Case study : Results – Cumulated release of Cr_{total}



Case study : Ecotoxicological results



Case study : Ecotoxicological results



Case study : Conclusions

- Exemplarity of the scientific approach (full application of EN12920, integration of all steps and disciplines)
- The effect of the hydric regime has been demonstrated : the mobilization of the pollutants is more efficient in real conditions of exposure (residence time more important and more time for equilibration between each humidification event) compared to lab scale behavior (permanent high water flow)
- Efficiency of the lysimeters scale for taking into account the specificity of the hydrodynamics of the scenarios and the fitting of the model parameters

Multiple-scale dynamic leaching of a municipal solid waste incinerator ash

D. Guyonnet, F. Bodéan, G. Brons-Laot, A. Burnol, M. Crest, J. Méhu, P. Moszkowicz, P. Plantone



Réunion Limule du 21 janvier 2005

Context & objectives

- Acceptance of waste management practices (reutilization, landfill, ...) requires an understanding of waste behaviour during leaching.
- Standardized laboratory tests are proposed to provide information on pollutant emission from waste during leaching (for ex. prCEN/TS 14405).
- How do we extrapolate from laboratory conditions to field conditions ?
- In particular, what are the possibilities and limitations of an extrapolation via the liquid/solid ratio: $LS = l t / (d h)$?
- To help answer such questions, the BRGM, in collaboration with INSA-Lyon and ADEME, initiated the LIMULE project (Multiple-Scale Leaching).

Source-Term Workshop, Paris 2006

> 2

Studied waste

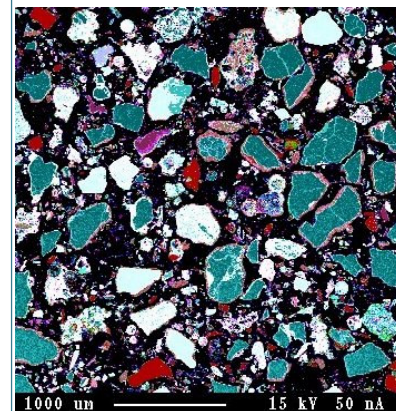
Boiler ash from a fluidized bed MSW incineration plant



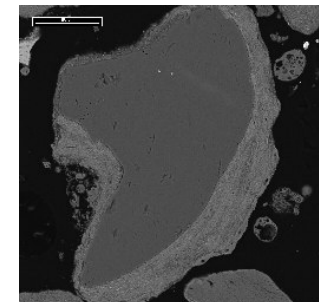
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Mineralogical analyses



grey = quartz
white = Al, K, Na silicates
purple = Fe oxydes
red = Ca phosphate

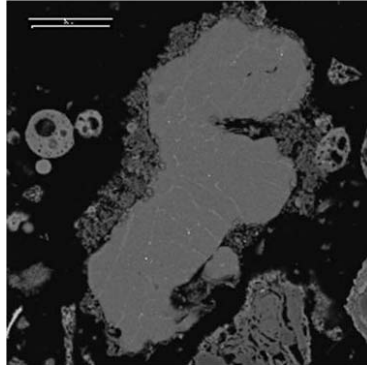


Ca-coating of quartz grains

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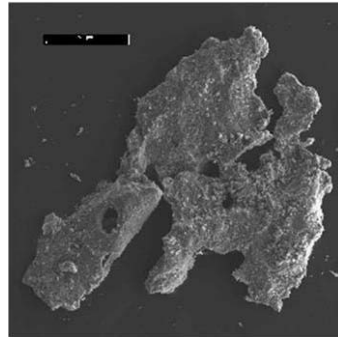
> 4

Mineralogical analyses (cntd.)



SEM photograph of Aluminum metal in thin section.

1.4% Aluminium metal in the solid



Aluminum metal particle

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3 scales were investigated

Scale 1 : laboratory scale (upflow percolation test)



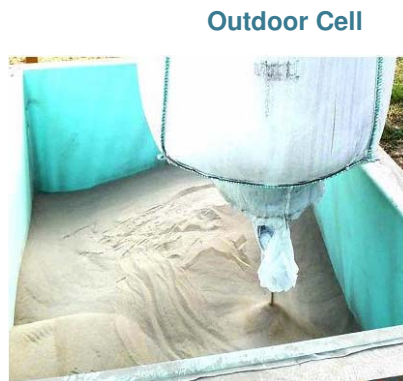
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Scale 2 : lysimeter cells



Indoor Cell



Outdoor Cell

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Scale 3 : large column



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Scales and percolation rates

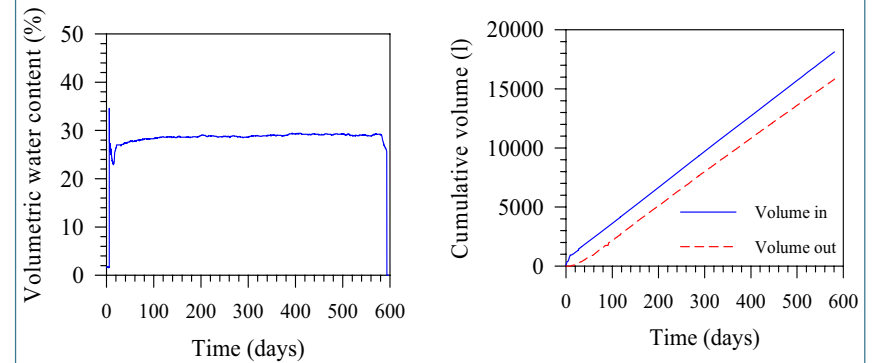
Scale of experiment	Infiltration (cm/day)	Infiltration conditions	Duration
1: Upward-flow percolation column (30 cm)	15	Controlled	60 days
2: Indoor lysimeter cell (1 m)	0.55	Controlled	590 days
2: Outdoor lysimeter cell (2 m)	0.11 on average	Uncontrolled	610 days
3: Large column (5 m)	3.8	Controlled	580 days

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Hydraulic data

- Data from large column show steady-state conditions (30 l/day injected).

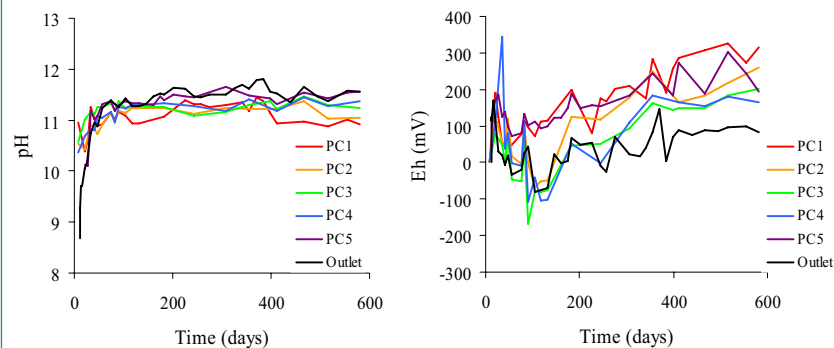


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Chemical data

- pH and Eh

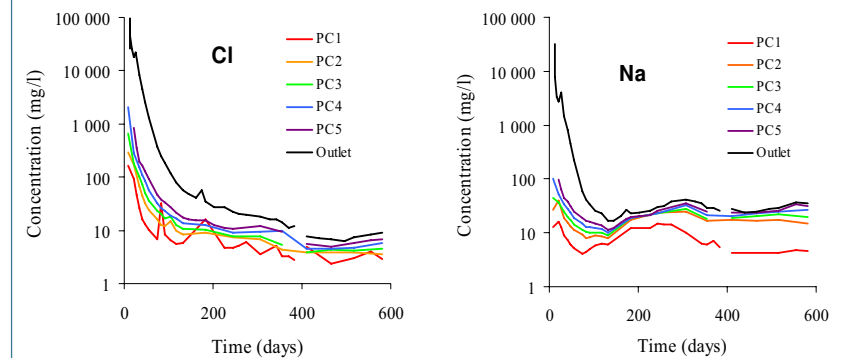


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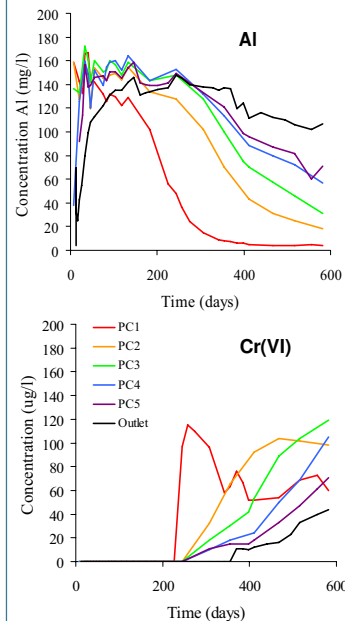
Concentration vs. time data

- Non reactive constituents: typical dilutional behaviour



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Concentration vs time data (cntd.)

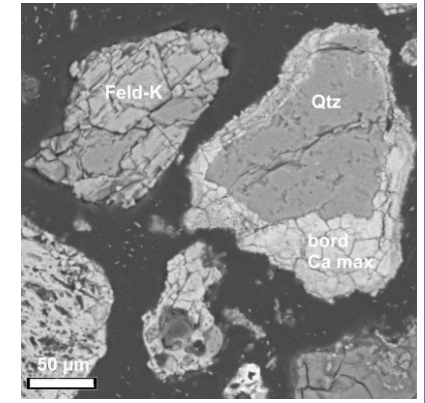
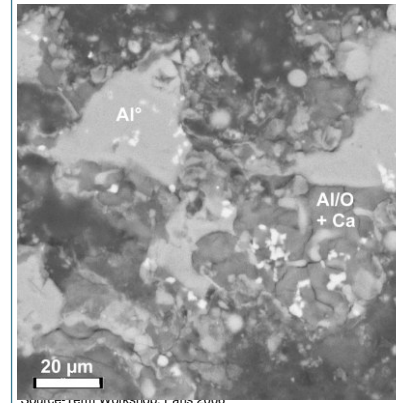
- Reactive constituents; here Al and Cr(VI) show coupled behaviour.
- Suggests coupling between oxidation of Al^0 and reduction of Cr(VI) to Cr(III)
- Also suggests kinetic effects

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Mineralogical analysis after leaching

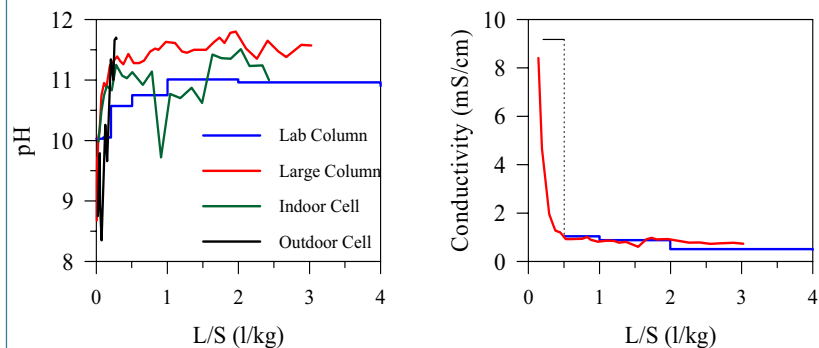
- Al metal is attacked, with precipitation of Al hydroxides

- Quartz grains are also attacked



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Concentration vs. LS data and comparison between scales

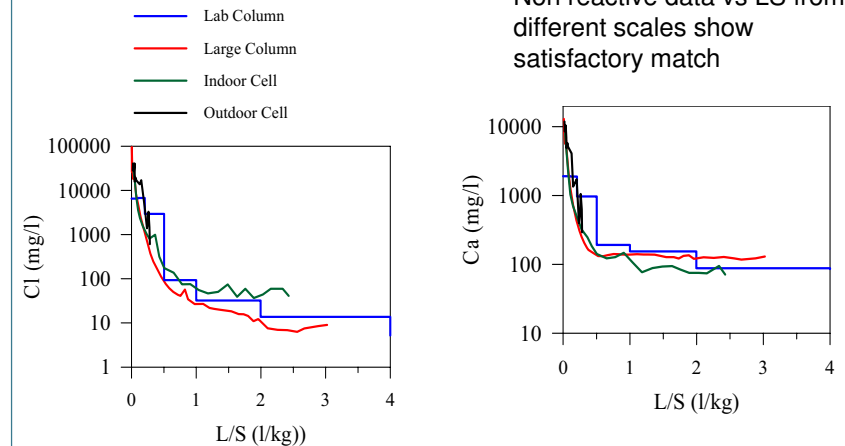


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Concentration vs LS data: non-reactive constituents

- Non reactive data vs LS from different scales show satisfactory match

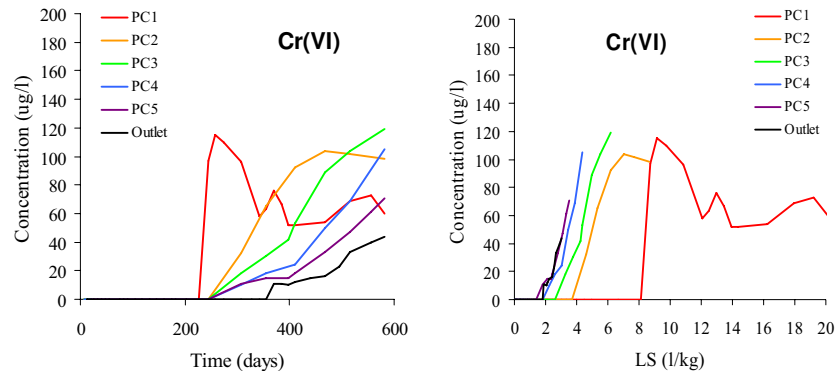


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Concentration vs LS data: Cr(VI) in large column

- Plotting vs LS decreases match between data

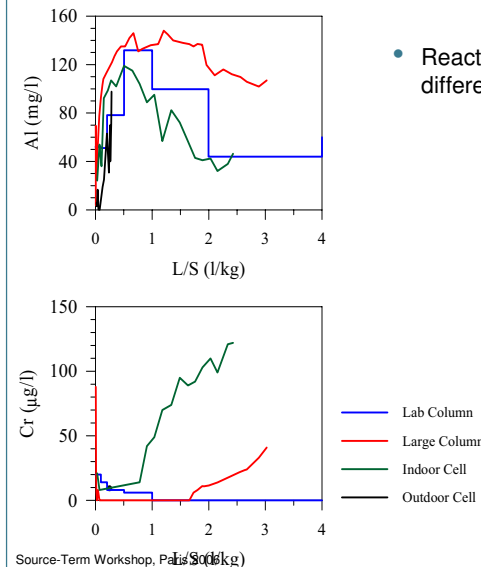


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Concentration vs LS data: reactive constituents

- Reactive constituent data vs. LS from different scales: no satisfactory match

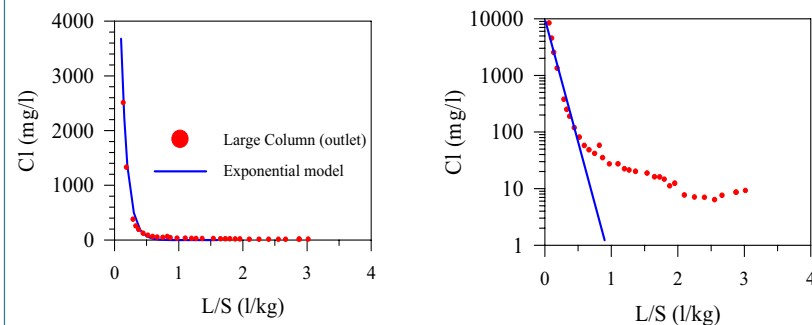


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Modelling, non-reactive constituents

- Even for non-reactive constituents, exponential model was unable to reproduce data (tails)



- For extrapolation: better to use directly the lab C vs. LS curve

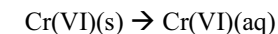
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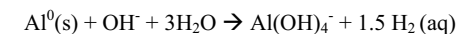
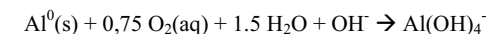
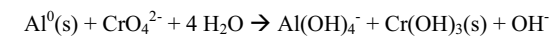
Modelling. Reactive constituents

- Based on observations and previous studies (Astrup et al.):

- kinetic dissolution of Cr(VI):



- Al^0 oxidation by Cr(VI), O_2 and/or H_2O :



- Kinetic control on redox reactions:

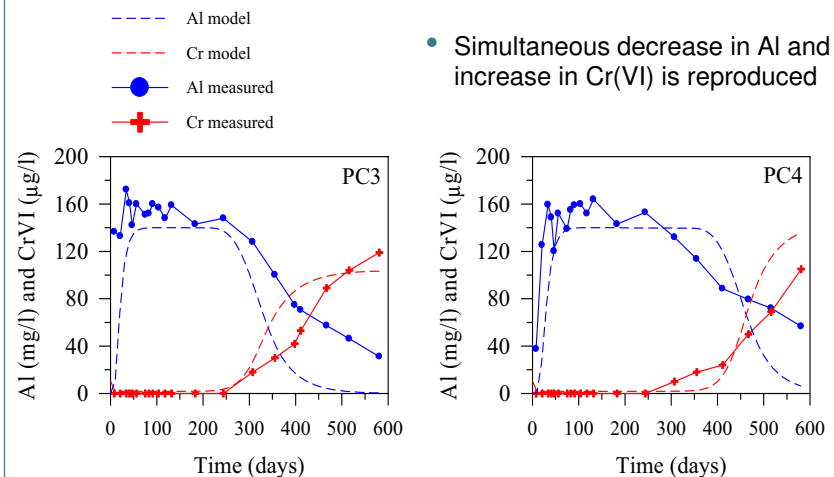
$$\frac{d(\text{Al}^0_r)}{dt} = -k_{\text{Al-ox}} (\text{Al}^0_r / M_0)^p [\text{O}_2(\text{aq})]^q$$

$$\frac{d(\text{Cr(VI)(aq)})}{dt} = k_{\text{Cr-s}} - k_{\text{Cr-red}} [\text{Cr(VI)(aq)}] \text{Al}^0_r$$

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Modelling. Reactive constituents (cntd.)



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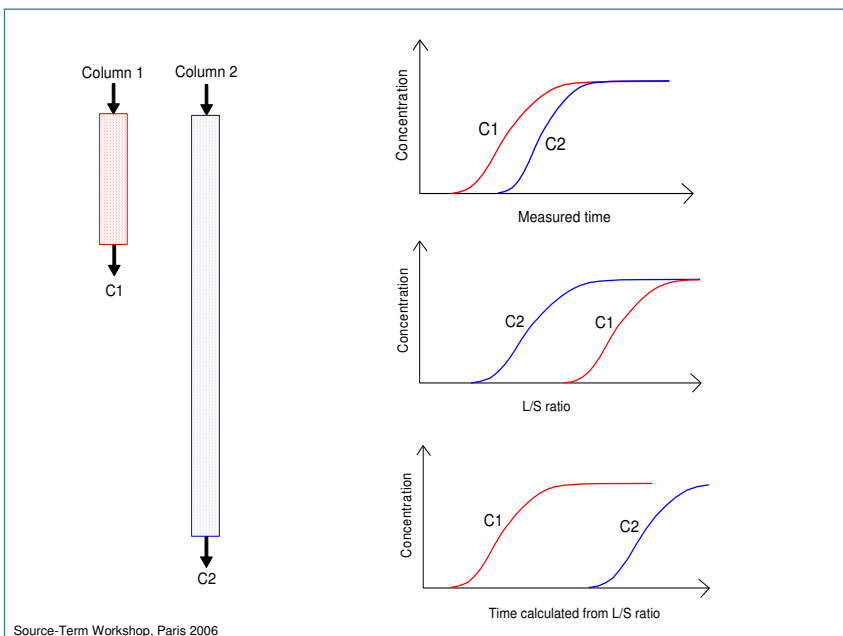
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Conclusions

- For non-reactive constituents (soluble salts: Cl, Na, Ca, K, ...), the LS ratio was found to be a satisfactory correlation parameter and we could use it for extrapolation between scales and flowrates.
- For reactive constituents, such as Al, Cr, the LS ratio did not provide a means of extrapolation due in particular to kinetic effects.
- If kinetic effects dominate, extrapolating from lab scale to large scale with the LS ratio will tend to overestimate breakthrough times.

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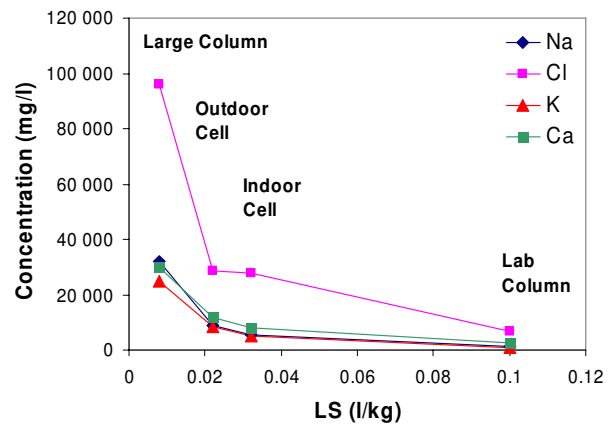
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Conclusions (cntd.)

- The exponential decay model (perfectly stirred + continuously diluted reactor) did not provide an adequate fit to measured data (use lab C vs. LS curve directly).
- Coupled transfer-chemistry modelling provided very valuable insight into the behaviour of the system.
- Given the very large number of controlling variables, predictive capability is however questionable.
- For soluble constituents, first concentrations obtained from lab column (LS = 0.1) were found to be much lower than first concentrations from other experiments (definition of C_0 ?)

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- Need to perform tests at different scales to extrapolate to meaningful LS for problem at hand ?

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THANK YOU FOR YOUR ATTENTION

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General Conclusions

- Leaching Assessment should be viewed as an integrated system
 - All assessments are simplifications and estimates of field performance
 - Key processes and conditions need to be clarified through iterative evaluation of lab and field studies
 - Field scenarios need to be defined and agreed upon as acceptable approximations for specific applications
 - Laboratory tests for identification and quantification of specific processes and intrinsic parameter estimation – not direct mimic of field conditions
 - Modeling is necessary step to translate laboratory testing to field scenarios

- 
- Field conditions are complex
 - Spatial gradients vary in response to episodic events (e.g., precipitation)
 - Understanding boundary conditions is critical
 - Understanding contaminant behavior requires understanding
 - Wide range of constituents (cations, anions, DOC) and chemical conditions (pH, ionic strength, redox) – coupled chemistry
 - Saturated and unsaturated conditions
 - Distribution of and processes within aqueous, gas and solid phases and at their interfaces – kinetics and equilibrium states
 - Evolution of the solid matrix (physical and chemical)



Scientific Understanding serves as the basis for Management Decisions

- Research defines key processes, conceptual models and simulations
- Research based, detailed understanding must be simplified to for routine decisions
 - Retain most important processes
 - Standardize data gathering, testing, data evaluation, scenario modeling, and decision basis
 - Uncertainty should be identified, including sources and estimate of magnitude – example: accuracy and precision of lab test – interlab comparisons



Most Critical Needs

- Laboratory to field comparisons and assessment system validation – coupled with water balances and system description; primary & secondary materials, disposal
- Standardized Assessment & Application Guidance for implementation
 - Scenarios, testing, modeling, data presentation, decision basis, quality control (for all aspects)
- Fundamental data and constitutive relationships for key processes
 - Thermodynamic constants for key mineral phases at relevant conditions
 - Kinetic parameters for key reactions and phase changes (when materials & processes never reach equilibrium)
 - Behavior and impacts of variable moisture (water retention curves, gas and liquid phase diffusivity, activity)
 - Carbonation rates & extent as a function of material and conditions
 - Physical & chemical evolution of parent materials



Which systems should we focus on?

- Materials?
 - Cements, bottom ash, coal fly ash, APC residues
- Scenarios?
- Risk-driving constituents?



Additional considerations

- Need to include organic constituents
- Products – current product evaluation
- Scenarios – roadbase; landfill (barriers?); surface impoundments, monolith landfills – flow patterns and crack development; embankments
- How to assess durability? Criteria?
- LCA? What? How? Why?
- Other emissions? Bioavailability? Dust?
- Use of long-term natural analogues leading to methods evaluation & improvement
- Need to understand from material capacity & performance rather than starting with pollutants
- Reduce material variability



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