

EUG XI



Symposium AI03

Waste Solutions:
Environmental Questions,
Environmental Answers

Convenor

Jeremy Joseph

AI03 Waste Solutions

Sunday PO Session

AI03 : SUPO1 : PO Low-Rank Coals for Disposal of the Surfactant Waste Waters

Yilmaz Burkut (ordgeo@itu.edu.tr),
Vildan Esenli (esenliv@itu.edu.tr) &
Murat Budakoglu (budakoglu@hotmail.com)
I.T.U. Faculty of Mines, 80626 Maslak, Istanbul, Turkey

Disposal of low concentrate waste water solution of anionic (Na - dodecylsulfate), cationic (N - cetylpyridinium chloride) and non - ionic (Polyvinyl pyrrolidone) surfactants in order to reach the natural equilibrium conditions is one of the important problem for environment. Utilization of low - rank coals (including peats) for capturing of the mentioned diluted wastes is well - known process (Burkut, 2000). The purpose of this study is to investigate the bounding characteristics of various coal and peat samples collected from different areas in Turkey. Polished thin sections of fifty coal and peat samples were examined by polarizing microscope. In particular, two convenient samples picked - up and experimented laboratory for determination of the bounding properties (Burkut, 1988).

It was observed that samples containing humin, humic acid and resinite were found to be suitable for this purpose and the coals with aromatic molecular texture yielded low catching ability. Capture phenomenon for low - rank coal and peat develops mainly two ways; adsorption by ion - exchange process, especially cationic or anionic forms and formation of organic complex with particularly fatty acids and some other aliphatic compounds. In later, ion - capturing is thought to be realized selectively by resinite and with a lesser amount by vitrinite, exinite and other related maserals (Burkut, 1993).

The table below summarized of the average experimental results. Conclusions indicate that the catching (meq/gr) of low - rank coal and peat depends on their chemical compositions. Generally, pH of solutions are between 7 and 9.

Coal types peat Low - rank coal Area Yeniçaga (meq / gr)
Alpagut - Dodurga (meq / gr) Anionic surfactant 1.23 1.06
Cationic surfactant 1.04 0.83 Non - ionic surfactant 0.04 0.03

Burkut Y, *TUBITAK MAG :602 (in Turkish)*, 200 p, (1988).
Burkut Y, Suner F, Gultekin AH, *EUG VII Strasburg*, 5, 635, (1993).
Burkut Y, *DPT Project No: 50/94K (in Turkish)*, 145 p, (2000).

AI03 : SUPO2 : PO The Effect of Additive on the Long Term Stability of Boiler Ashes and Gas Cleaning Residues of Municipal Solid Waste Incinerator

**Soraya Heuss-Abbichler, Hans Werner Schmidl
& Wolfgang Spiegel**
CheMin GmbH, Am Mittleren Moos 48, 86167 Augsburg,
Germany

The effect of additive on the long term stability of boiler ashes and gas cleaning residues of municipal solid waste incinerator

The deposit of boiler ashes BA and gas cleaning residues GCR of municipal solid waste incinerators (MWSI) in monfills sets a problem due to high concentrations of salt and heavy metals. The residues have to be classified as hazardous waste as the content of leachable components especially Pb exceeds the regulatory limit of 5 mg/l. The analyses of leakage water of a monofill for MSWI-ashes in Bavaria, however, delivered leaching properties being less harmful than expected. Phase analyses of altered residues of the monofill exhibit high contents of ettringite. Microprobe analysis depict high concentrations of both heavy metals like Cu, Pb, Zn and of chlorine in these phases. These observations suggest that the retention capacity of the altered residues concerning soluble components is caused by the growth of reservoir minerals. Two different sets of experiments were conducted at 30°C and defined water contents. The one set of the experiments was carried out using solely BA and GCS. Aim of this study was to determine the kinetics of the ageing processes in this material. The phase relations in the samples were determined by the means of x-ray diffraction and microprobe analyses. Leaching experiments were carried out in order to

determine the fixation properties of the residues. The aim of the second set of experiments was to develop a treatment procedure of BA and GCR in order to accelerate the growth rates of reservoir minerals and thus to enhance the retention capacity of the deposits with respect to salts and heavy metals. Five different waste recycling materials with high aluminium concentrations were selected. Mixtures of these additive with the residues BA and GCS were prepared and the samples were heat-treated up to 100 days. First results of leaching experiments show that in some specimens the salt content of the leachate is reduced and that the amount of soluble heavy metals is much lower than the determined values for residues without additives. Phase analysis indicate higher contents of reservoir minerals as ettringite. According to these results the residues may be stabilised and the leaching of the heavy metals and chlorine may be reduced by changing the bulk composition of the residues in order to improve the growth conditions for reservoir minerals.

AI03 : SUPO3 : PO Daily Dissolved Cadmium Fluxes in the Lot- Garonne Fluvial System (France)

Stéphane Audry (s.audry@geocean.u-bordeaux.fr),
Gérard Blanc, **Yvon Lapaquellerie** &
Noële Maillat
Université Bx I. DGO, Avenue des Facultés, Talence
33405 CEDEX, France

Daily survey of Lot and Garonne river discharge and total suspended sediment content (TSS) were obtained for 1990-1998 period. This decade included contrasting hydrologic cycles and appears representative over a longer period of time (i.e. 1959-1998). High frequency analyses of dissolved and particulate cadmium concentration allow us to calculate annual dissolved and particulate cadmium fluxes. Daily dissolved cadmium fluxes were also computed. That allowed us to propose an accurate dissolved cadmium balance for the Lot-Garonne man-polluted fluvial system (8400 km²). Dissolved cadmium fluxes range from 0.03 kg.day⁻¹ to 16 kg.day⁻¹ and from 0.3 kg.day⁻¹ to 23 kg.day⁻¹ for the Lot and Garonne river, respectively. This study indicates a 66% decrease of total cadmium fluxes from the Lot river between 1990 and 1998. This decrease is probably due to the lowering of the punctual anthropogenic input deriving from the man-made isolation of the Decazeville manufacturing waste area. Thus, the fluvial system reached up a stationary state which provides information about the relation between climate and metal transport. Consequently, since 1992, upstream Garonne appeared to play a key role within cadmium fluxes patterns, such as dilution role within humid years and enhancement role within dry years. River water discharge and daily dissolved cadmium are linked by linear relationship having different slopes as a function of TSS water content. Furthermore, dissolved cadmium fluxes are not related to water discharge intensity but rather to high water and flood distributions along the year. Thus, dissolved cadmium fluxes variability is a function of climate variability within the basin scale.

AI03 : SUPO4 : PO Metal Mobilization in the Fluid Mud of the Gironde Estuary (France) in Low Discharge Regime

Sébastien Robert (s.robert@geocean.u-bordeaux.fr)¹,
Gérard Blanc (g.blanc@geocean.u-bordeaux.fr)¹,
Gwénaél Abril (i5gw@civil.auc.dk)² &
Gilbert Lavaux
(g.lavaux@geocean.u-bordeaux.fr)¹
¹ DGO. Université Bordeaux I, Avenue des Facultés,
33405 Talence CEDEX, France
² Department of Civil Engineering, Environmental
Engineering Laboratory, Aalborg Universitet,
Sohngaardsholmvej, 57 9000 Aalborg, Denmark

Concentrations of Cd, Cu, Cr, Fe, Mn, Ni, Pb in particulate and dissolved phases were performed by AAS and ICP-MS along the water column- Maximum Turbidity Zone (MTZ)-Soft Mud (SM)- concrete sediment system at water slacks during low water discharge period. With measurements of salinity, dissolved oxygen, nitrates, nitrites and ammonium, it appears spatial and temporal changing of physico-chemical conditions characterized by the superposition of two diagenetic sequences occurring in the MTZ- SM system and in the upper part of the concrete sediment, respectively. Hence, heterotrophic activity exists in the MTZ-SM system and in the deposited sediment. In this latter zone, transient

metallic profiles are observed because of the cyclic presence of oxygen and slow reduction kinetics. In the MTZ-SM system, three oxidants occur (dissolved oxygen, nitrates, Mn and Fe oxo-hydroxides), with releasing of metals (1.4 nmol/l of Cd) at the base of the SM layer which seems to last over the tidal cycle. Correlation coefficients determination between metal particulate concentrations show qualitatively the adsorbing affinity of the studied metals under the sampling conditions. The metals can be classified in two families: those which are solubilized under anoxic conditions (Mn, Cd, Ni, Pb, perhaps Fe) and those which are solubilized under oxic conditions (Cu, Cr). The MTZ-SM can be considered as a dynamic integrator of the tidal cycles and could constitute a source of dissolved metals in the Gironde Estuary.

AI03 : SUPO5 : PO Observation of the Fluvial Input of Suspended Solids, Particulate Organic Carbon and Cadmium into the Gironde Estuary (1990-1999)

Jörg Schäfer (j.schaefer@geocean.u-bordeaux.fr),
Gérard Blanc (blanc@geocean.u-bordeaux.fr),
Yvon Lapaquellerie, **Noële Maillat**,
Eric Maneux (maneux@geocean.u-bordeaux.fr) &
Henry Etcheber (etcheber@geocean.u-bordeaux.fr)
Université Bordeaux I, DGO UMR CNRS 5805 EPOC,
Avenue des Facultés, 33405 Talence CEDEX, France

An intensive long-term observation of suspended solids (TSS), particulate organic carbon (POC) and cadmium transported into the Gironde estuary (France) by its major tributaries has been carried out in 1990-1999. This decade included contrasting hydrologic cycles and appears representative for a much longer period (1959-1999). The main tributaries of the Gironde estuary, the Garonne and the Dordogne river systems have been observed separately and compared. Although the Garonne river system has been more seriously polluted by mining and some industrial activities (e.g. with Cd), its natural run-off character is less modified than that of the Dordogne river system, where a number of large dams largely inhibit annual variations of discharge and fluxes. Consequently, the discharge of the Garonne is more related to the hydrology of the whole draining basin and the fluxes of water and particulates show higher temporal variations in the Garonne river system. As POC and particulate Cd are associated to suspended matter and their concentrations are much less variable than turbidity, their fluxes are mainly controlled by the TSS-transport. Especially during floods, close observation of discharge and TSS concentrations is necessary, as a major part of annual fluxes of TSS and associated pollutants may occur within few flood days. Succession of dry and wet years also has a significant influence on annual particulate fluxes, especially for less regulated systems like the Garonne. Fluvial inputs into the Gironde have been calculated as the sum of fluxes transported by the Garonne and the Dordogne river systems. Mean annual fluxes into the Gironde observed in 1990-1999 are about 3.4 .10¹⁰.m³.yr⁻¹ for river water, 3.24 .10⁶.t.y⁻¹ for suspended solids (TSS) and 1.19 .10⁵.t.y⁻¹ for particulate organic carbon (POC). Generally, the contribution of the Garonne river system dominates the fluxes into the Gironde (river water, TSS, Cd). Nevertheless, in dry years the mean contribution of the Dordogne river system to the POC input into the estuary exceeds that of the Garonne reflecting significant differences in vegetation and soil due to natural properties and land management of the basins. Fluxes of total Cd into the estuary are about 12.4 t.y⁻¹ of which 2.2 t.y⁻¹ are transported in the dissolved and 10.2 t.y⁻¹ in the particulate phase, respectively.

AI03 : SUPO6 : PO Influence of Natural and Anthropogenic Sources on Heavy Metal Distribution in Urban Soils- A Case Study from Palermo (Sicily), Southern Italy

Daniela Salvagio Manta (salvagiod@libero.it)¹,
Massimo Angelone (angelone@casaccia.enea.it)²,
Adriana Bellanca (bellanca@unipa.it)¹ &
Rodolfo Neri (neri@unipa.it)¹
¹ Dipartimento di Chimica e Fisica della Terra C.F.T.A.
Università di Palermo, Via Archirafi, 36, 90123
Palermo, Italy
² ENEA, TEIN CHIM, C.R. Casaccia, P.O. Box 2400,
00100 Roma, Italy

Heavy metals have received increasing attention as toxic pollutants in urban areas, their main anthropogenic sources including industrial activities, coal burning, refuse inciner-

ation, vehicle emissions and building construction. Concentrations of heavy metals in 100 topsoil samples collected in green areas and public parks within the city of Palermo have been determined to provide information on specific emission sources. Soils show pH(H₂O) from 7.22 to 8.25, CEC from 5.0 to 55.8 meq 100 g⁻¹ and a mineralogical composition dominated by carbonate, quartz, clay minerals and feldspar. All soil samples were analysed for total Pb, Cd, Cu, Zn, Ni, Co, Cr contents by ASS and GFASS, following aqua regia digestion. Hg values were measured by Direct Mercury Analyzer-80 (Milestone Inc., Monroe CT). The data obtained (as mg Kg⁻¹) range as follows: Cd from 0.35 to 1.9, Cr from 12 to 63, Cu from 10 to 121, Ni from 3.1 to 30.5, Pb from 30 to 443, Zn from 50 to 318, Co from 1.4 to 13.6, Hg from 0.02 to 6.8. Statistical analysis and mapping techniques evidence a dominant anthropogenic input for some metals. Pb concentrations on average exceed background levels by a factor of 10, the highest concentrations generally occurring in sites close to main roads with heavy traffic. Zn and Cu spatial distributions are very similar to that of Pb, suggesting the same source for these elements. Ni, Co, Cr values are compatible with their average contents in unpolluted soils of Sicily. Owing to Cd being an uncommon element in rocks and soils (0.2 mg Kg⁻¹ or less), its high levels in Palermo topsoils, should be attributed to the impact of human activity. However, remarkably high concentrations of Cd have been measured in some bedrocks in Palermo (1.6 mg Kg⁻¹) and in rural Alfisols and Mollisols (up to 2.4 mg Kg⁻¹) in Sicily. A significant correlation between Cd and Mn values in the topsoils is interpreted as indicative of an important lithogenic effect on the Cd distribution. In some sites the soils are markedly enriched in Hg by a factor of about 100 with respect to rural soils in Sicily, suggesting that the metal is given off in fumes from industries and chemical laboratories and rapidly fixed in the soil.

AI03 : SUpo07 : PO
Assessment of Stability of Rock Massif for
Disposal of Radioactive Waste

V. N. Tatarinov (victat@wdcb.ru) &
M. V. Tatarinov
117296 Moscow, Molodeznaja str. 3, Russia

It is well known that one of the most difficult ecological problems is the permanent safe disposal of high-level radioactive wastes (HLRW) and fulfilled nuclear fuel in deep geological formations. Prediction of geomechanical and hydrogeological processes in rock massifs under high pressures, temperature, and radiation near underground storages and repositories of HLRW is the fundament basis for ecological risk assessment.

The safety of HLRW disposal depends on the natural isolation properties of the geological medium and the stability of its natural factors which determine the persistence of these properties with time. Selecting most stable geologic blocks in the territory of Russia to dispose of HLRW includes a number of problems, therefore our research aims at solving the following problems: selecting most suitable long-term crustal areas on the basis of assessment (rating) of geological medium (its properties, conditions and processes) with account for geodynamic factors of the area; prediction of stability and resistance of the geological medium of individual crustal areas, risk assessment of destabilization of the medium for the whole term of HLRW occurrence in it; prediction of the natural isolation properties of the rock massif during construction and exploitation of HLRW repositories under the effects of geomechanical processes. At the first stage of the research the major problem is the one of defining marginal parameters (criteria) to assign one or another site to the above-mentioned groups. When materials of various kinds, which frequently are not expressed numerically, are analyzed an expert opinion may be applied to make decision on regional scale.

To achieve this natural factors are divided into three groups: factors characterizing the internal properties of rocks and blocks; factors characterizing the external active effects on the block; factors determining the dynamics of the processes in the structural block.

The following step after assigning each factor to a group and giving them expert estimate is the combined assessment of the total of factors and making a decision about the suitability of structural blocks for HLRW repositories construction. Separate factors are assumed to influence independently on one another.

The third stage of the research involves elaborating the assessment technique of rock massif isolation properties under high temperatures and rock pressure.

AI03 : MOam02 : F1
Weathering of Slag Materials

Dieter Rammlmair (rammlmair@bgr.de)
BGR, Stilleweg 2, D-30655 Hannover, Germany

Slag material from smelters after deposition on a heap is exposed to weathering and to diagenetic processes. Weathering is a process controlled by the availability of water, the climatic conditions, the chemical and mineralogical composition of the material, the sedimentological background, the microbial activity and time. Weathering of slag material induces significant changes of surface conditions culminating in the decomposition of glass or available mineral phases. Selective leaching, shrinking core dissolution or protective coating are expressions of such changes, and they are basically responsible for the surface area, pore size and pore shape development in a slag heap. A development which is not homogeneous within a heap, nor constant through time. One the one hand a macro pore system might develop providing a pathway for preferential mine drainage, on the other hand the water down flow in such a system can be retarded due to an elevated retention capacity and enhanced surface roughness and finally an enhanced capillary transport is accompanied by precipitation of secondary phases along the water- air boundary layer oscillating in thickness according to the climatic premises. Precipitated matter might be partially soluble and become re-incorporated into the solution after rainfalls and being reintroduced into the slag heap system feeding both the micro and macro pore flow. Whilst the micro pore flow provides slow downward movement with elevated reaction times the macro pore flow is a rapid down flow responsible for mine drainage and subsequent contamination of the surroundings. In a favourite climatic environment the capillary upward movement might be the dominant feature being responsible for the formation of hard pan covers reducing the water input, enhancing the grain agglutination and providing a protective cover to the heap being responsible for changes of quantity and quality of the mine drainage system. This paper focuses on the influence of weathering and diagenesis in the uppermost portion of a multi-component slag heap from an arsenic production side and from a Ni-Cu-smelter slag showing rapid changes in dissolution and precipitation style and rate according to the climatic conditions ranging from moderate to semi-arid, respectively.

AI03 : MOam04 : F1
Stability of Mineralogical Assemblages in
Municipal Solid Waste Incinerator (MSWI)
Bottom Ash: An Experimental Study

Nathalie Delville (delville@opgc.univ-bpclermont.fr)¹,
Jean-Marc Montel (montel@cict.fr)² &
Pierre Boivin (boivin@opgc.univ-clermont.fr)¹
¹ Université Blaise Pascal, 5 rue Kessler, 63000 Clermont-Ferrand, France
² Université Paul Sabatier, 39 allées Jules Guesde, 31000 Toulouse, France

MSWI bottom ash are commonly used for road construction, despite the fact that it is difficult to predict the long-term evolution of both their mechanical characteristics and leaching potential. The main components of MSWI bottom ash are: a vitreous matrix resulting from quenching of a silicate liquid, pseudo-mineral crystallised phases, metallic blending quenched droplets and carbonaceous residues. This assemblage is highly reactive, and its long-term behaviour depends on both the evolution of each of these components and their mutual interactions. In order to constrain the starting point of the long-term evolution of MSWI bottom ash, we experimentally studied the formation of the starting mineralogical assemblages by remelting an MSWI bottom ash under controlled conditions.

The starting product is a fresh bottom ash came from a facility fit out with a rotary kiln. Its bulk chemical composition (in weight: SiO₂=53%; Al₂O₃=11%; Fe₂O₃=8%; MgO=2.5%; CaO=16%; Na₂O=6.3%; K₂O=1.4%) is similar to other European bottom ashes (Bäverman et al., 1997; Freyssinet et al., 1998; Eypert-Blaison et al., 2000). Experiments were conducted at one atmosphere, between 1000 and 1300°C, under low (IW buffer) and high (air) oxygen fugacity. The experimental technique is derived from previous studies on basaltic system. With this procedure, chemical equilibrium is reached and no modifications occur during quench. The experimental products were studied by optical microscope, SEM, and electron microprobe.

For both oxygen fugacity conditions, the liquidus is close to 1170°C and the solidus is below 1000°C. Around 1050°C, few metallic alloys were not melt. At IW, the 1000°C assemblage is made of glass, wollastonite, clinopyroxene and plagioclase. In air, the 1000°C assemblage is also made of glass, clinopyroxene, wollastonite, plagioclase plus apatite. The IW assemblages and the minerals compositions are almost identical to those observed in bottom ash. On the contrary, in air, there are several differences: Clinopyroxenes are ferroaugite instead of salite and high-temperature apatites are formed, which have never been identified inside bottom ash.

Despite apparent heterogeneity of the starting bottom ash and uncertainties about the fabrication conditions, we find a surprisingly good agreement between the observed mineral assemblages and the experimental products for IW conditions. Moreover, the phases compositions are also very similar. This work demonstrates that conditions close to chemical equilibrium prevail during the bottom ash fabrication process.

Bäverman C, Sapiej A, Moreno L & Neretnieks I, *Waste Management and Research*, **15**, 55-71, (1997).
Freyssinet P, Piantone P, Azaroual M, Itard Y, Clozel B, Baudron JC, Hau JM, Guyonnet D, Guillou-Frottier L, Pillard F & Jezequel P, *Evolution chimique et minéralogique des mâchefers d'incinération d'ordures ménagères au cours de la maturation*, BRGM, **280**, (1998).
Eypert-Blaison C, Yvon J, Lhote F & Kohler A, *Les techniques de l'Industrie Minérale*, **6**, 40-52, (2000).

AI03 Waste Solutions

AI03 : MOam05 : F1 Thermodynamic Stability of Waste Glasses

Didier Perret (didier.perret@dplanet.ch)¹,
Jean-Louis Crovisier (jlc@illite.u-strasbg.fr)²,
Peter Stille (pstille@illite.u-strasbg.fr)²,
Graham Shields (gshields@science.uottawa.ca)³,
Urs Mäder (urs@mpi.unibe.ch)⁴,
Thierry Advocat (advocat@amandine.cea.fr)⁵,
Kaarina Schenk
(kaarina.schenk@buwal.admin.ch)⁶ &
Marc Chardonens
(marc.chardonens@buwal.admin.ch)⁶

¹ Université de Lausanne, Institut de Chimie Minérale et

Analytique; BCH, CH-1015 Lausanne, Switzerland

² ULP Ecole et Observatoire des Sciences de la Terre
CNRS, Centre de Géochimie de la Surface UMR 7517;
1, rue Blessig, F-67084 Strasbourg Cedex, France

³ University of Ottawa, Carleton-Ottawa Geoscience
Centre; 365 Nicholas Street, Ottawa Ontario K1N 6N5,
Canada

⁴ Universität Bern, Mineralogisch-Petrographisches
Institut; 1, Balzerstrasse, CH-3012 Bern, Switzerland

⁵ CEA Marcoule, Service de Confinement des Déchets;
BP 171, F-30207 Bagnols sur Cèze Cedex, France

⁶ Swiss Agency for Environment, Forests and Landscape,
Division Waste, CH-3003 Bern, Switzerland

The high-temperature treatment of municipal solid wastes and their associated residues (bottom ash, fly ash, filter cake, optional wastes) is a promising alternative to the remaining problem of residues from conventional incineration. The end products of high-temperature processes are characterised by glassy matrices that can render inert non-negligible amounts of heavy metals. As the quality of such "waste glasses" is higher than that of conventional residues, they could be buried at landfill sites for inert materials or possibly reused for civil engineering purposes (e.g. road construction). For the in-depth revision of the regulations on waste management in Switzerland, the Swiss Agency for Environment, Forests and Landscape has initiated a broad survey of high-temperature treatment processes. A series of 23 samples from different processes, representing a range of operating conditions, and 3 standards, were studied thoroughly. Their physico-chemical characteristics and their behaviour during severe leaching experiments were determined. In addition, the thermodynamic stability of these glasses was estimated by calculation of their free energy of hydration ΔG_{hydr} . For samples that are vitreous or vitrocristalline, it is shown that Si and Ca content control the thermodynamic stability, and that neither heavy metal content, type of incineration process nor nature of the incinerated material is significant in this regard. Si ($[\text{SiO}_2] = 25.1\% - 56.0\%$; mean = $41.2\% \pm 8.3\%$) directly influences the durability of the samples, while Ca ($[\text{CaO}] = 3.9\% - 37.6\%$; mean = $22.4\% \pm 8.9\%$) governs the pH of the leachate during corrosion, which in turn affects the thermodynamic stability. It is also clearly confirmed that there is a close inverse relationship between the calculated thermodynamic stability of the samples and their experimental rates of dissolution under aggressive conditions of corrosion. Attempts to compare our results with the large literature database for nuclear high-level waste glasses, their proxies and other analogues (ancient and commercial glasses) are limited by technical restrictions (sample form: block vs. powder). Nevertheless, it is demonstrated that the behaviour of municipal "waste glasses" is similar to that of nuclear waste glasses, and that the calculated thermodynamic stability of municipal "waste glasses" can be used to estimate their relative quality and long-term durability.

AI03 : MOam08 : F1 The Langoya Gypsum Landfill and its Suitability to Store Inorganic Waste

Jens Jahren (jens.jahren@geologi.uio.no)¹,
Per Aagaard (per.aagaard@geologi.uio.no)¹,
Wenche M. Olsen¹, **Tor Loeken**² &
Trygve Sverreson³

¹ Dept of Geology, Univ. of Oslo, P.O.Box 1047 Blindern,
N-0316 Oslo, NORWAY

² NGI, P.O.Box 3930 Ullevaal Stadion, N-0806 Oslo,
NORWAY

³ NOAH, Pb H, N-3081 Holmestrand, NORWAY

The gypsum landfill at the small island of Langoya was in 1991 selected as the Norwegian national storage facility for inorganic hazardous waste. The major waste product is gypsum sludge produced from neutralization of heavy metal contaminated sulfuric acid, from the titanium dioxide production at Kronos Titan in Fredrikstad, Norway.

Two features make the Langoya depot specially suitable to store most inorganic waste. The first, is the hydraulic barriere towards seaward flow and leakage, as the depot is located in an old limestone quarry, which has been excavated to a depth of 40 m below sea level, giving an inwards gradient. The second, is the geochemical barriere created by the gypsum sludge itself.

The production of the gypsum sludge involves, in addition to the limestone neutralization, a further pH increase by adding slaked lime, precipitating out ferrous hydroxide. Part of the ferrous hydroxide is oxidized in contact with air. The resulting geochemical environment makes the gypsum sludge a suitable medium to store most other inorganic wastes as well. It has stable redox conditions from the buffering of ferrous-/ferric hydroxide, a pH between 8 and 10, and at the same time large quantities of reactive surfaces of iron hydroxides. This prevents the formation of oxyanions and ensures effective adsorption of heavy metals. Speciation studies of heavy metals confirm this behavior. Heavy metals are found in either insignificant or undetectable amounts in the pore waters. We have also carried out experiments where petroleum coke embedded in concrete was stored in the sludge for 5 months. In this study both the gypsum sludge itself and petroleum coke embedded in concrete stored in the sludge were investigated.

This study has shown convincingly that the Fe-rich gypsum sludge produced at Langoya is a suitable host for storage of most inorganic wastes.

AI03 : MOam09 : F1 Seepage Water from Uranium Mining Dumps in Eastern Thuringia, Germany: A Hydrogeochemical Study

Jörn W. Geletnek (joern@geo.uni-jena.de),
Dirk Merten (merten@geo.uni-jena.de) &
Georg Büchel (buechel@geo.uni-jena.de)
Institute of Geoscience, FSU Jena, Burgweg 11, D-07749
Jena, Germany

The area of Gera-Ronneburg in the eastern part of Thuringia, Germany, was between 1950-1990 one of the largest uranium mining sites in black shales in the world. Since 1990 the remediation of the mining legacy is worked out by the WISMUT GmbH with financial support of the German government. The uranium mining dumps mainly consist of black shales, diabases and sandstones of Ordovician to Devonian age. These metasediment rocks contain up to 7 wt% of sulfides, 5-9 wt% of organic carbon, 30-60 ppm of uranium and a series of trace elements. This preliminary study investigates the influence of the oxidizing and acidic seepage water of one the dumps (Nordhalde) on valley sediments and creeks. The seepage water is enriched in heavy metals, uranium and Rare Earth Elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Using heavy metals and REE normalized to shale as tracers, several processes along different flowpaths e.g. dilution, (co)precipitation can be identified. The seepage water which has been studied for several years shows pH-values of 2-3 and high conductivities of about 12 mS/cm. High concentrations of SO_4^{2-} (12-14 g/l), Fe (1.3-2.7 g/l), Mg (1.2-1.4 g/l) and Ca (1 g/l) were found in the 0.45 μm filtrates of the seepage water. There are also remarkable high concentrations of Al (220 mg/l), Mn (150 mg/l), Zn (15 mg/l), Ni (15 mg/l), Cu (1 mg/l), U (1-3 mg/l) and REE (total: 3 mg/l). Typically, filtration is performed on-field with a pore size of 0.45 μm . In order to investigate whether the considered elements are truly dissolved or bound to particles and colloids filtration with different cut off-sizes (0.45 μm , 0.2 μm) was also performed. Furthermore, nanofiltration was applied using a cut-off diameter of about 2 kDalton. The patterns of the REE-concentrations in the 0.45 μm filtrates as normalized to Post Archean Australian Sedimentary (PAAS) Rock are characterized by strong middle and heavy REE enrichment as compared to the light REE. Although the concentrations differ, probably due to dilution, the shale-normalized REE-patterns of surface waters sampled near the dump, have exactly the same pattern as samples of seepage water. Thus, the normalized REE patterns point to the dump as contamination source.

AI03 : MOam10 : F1 In Situ Stimulation of Microbial Sulfate and Iron Reduction in an Acidic Mining Lake by Addition of Organic Substrate

Katrin Wendt-Potthoff (potthoff@gm.ufz.de),
Matthias Koschorreck (koschorreck@gm.ufz.de),
Rene Frömmichen (froemmi@gm.ufz.de),
Peter Herzsprung (herzsprung@gm.ufz.de),
Silke Kellner,
Andreas Lorke (andreas.lorke@eawag.ch) &
Walter Geller (geller@gm.ufz.de)
UFZ Environmental Research Centre, Brueckstr. 3a, D-
39114 Magdeburg, Germany

Acid mine drainage can be formed from various types of mines. In opencast lignite mining areas in Lusatia, Germany, lakes form in the open pits due to ascending groundwater. The resulting lake water resembles dilute acid mine drainage. In these acidic mining lakes microbial sulfate reduction is inhibited by low pH (below pH 3) and a lack of organic substrates. Stimulation of sulfate reduction by addition of organic substrates is a common strategy to remove acidity from acidic mine drainage. This principle was applied in enclosures in a lake under in situ conditions. Addition of a complex organic substrate (Carbokalk - a byproduct of sugar production) together with straw as a growth matrix altered the chemistry and microbiology of the lake sediment completely. Iron was reduced and microbial sulfate reduction in the surface sediment was stimulated to a rate of 163 $\text{nmol SO}_4^{2-} \text{ cm}^{-3} \text{ d}^{-1}$. Cell numbers of sulfate reducers increased by up to 100,000fold. As a result the pH of the sediment was raised from 2.5 above 6. However lake water chemistry was hardly affected by these changes. Possible problems of the applied technique for lake restoration are discussed.

AI03 : MOam11 : F1 Physico-Chemical Controls on Kinetics of Natural Attenuation of BTEX and Chlorinated Solvents

Olivier Atteia (atteia@egid.u-bordeaux.fr) &
Michel Franceschi (francesc@egid.u-bordeaux.fr)
EGID, 1 Allée Daguin, 33607 Pessac Cedex, France

Natural attenuation is presently under focus due to the high cost of polluted aquifer remediation. In this paper we focus on the different aspects of natural attenuation of organic contaminant in subsurface aquifers. Beside the physical aspects of dispersion and retardation, the role of chemistry in the degradation is detailed. In fact, numerous microorganisms able to degrade BTEX and chlorinated solvents have been identified but it has been shown that the kinetics of degradation mainly depend, in field conditions, on the supply of electron donors or acceptors. That is why the following points are detailed through this paper: - The analysis of the energy involved in redox reactions of degradation and the best chemical conditions of reaction development. - For a large set of published data, the relationship between field determined degradation kinetics and the redox couples present in sediments is examined. This allows to determine several typical field situations for which the degradation kinetics may differ by orders of magnitude. - The detailed analysis of the transport of redox couples in several field conditions shows that the renewing of such components is slow and occur mainly at the border of the contaminant plumes. This overview shall help to determine the conditions necessary to consider natural attenuation as a remediation strategy for a given site.

AI03 : MOam12 : F1 Determination of Chlorine Stable Isotopic Composition in Chlorate and Perchlorate

Magali Ader (m.ader@reading.ac.uk) &
Max Coleman (m.l.coleman@reading.ac.uk)
Postgraduate Research Institute for Sedimentology, The
University of Reading, Whiteknights, Reading RG6
6AB, u.k.

Chlorate and especially perchlorate are almost totally man made and are used as weed-killers and for manufacture of explosives. They are localised, but significant, pollutants of water and there is interest in tracing their sources for forensic purposes. Therefore, there is some value in being able to characterise them by their chlorine stable isotope compositions. In addition, there is the possibility that microbial degradation of these compounds might produce a significant isotopic fractionation. Therefore, monitoring extent of intrinsic (natural) remediation could be achieved

AI03 Waste Solutions

by measuring isotopic compositions of residual (per)chlorate and chloride produced; comparable to the approach shown by Coleman et al., (1999) for chlorinated hydrocarbon solvent degradation). There are established methods to determine $\delta^{37}\text{Cl}$ of chloride (Eggenkamp, 1994) and so we chose to convert chlorate and perchlorate to chloride. To do this we rediscovered old chemical analysis methods allowing their quantitative reduction into chloride. Chlorate solution is heated with ferric iron in concentrated sulphuric acid (Vogel, 1989). The quantitative reduction of perchlorate uses alkaline fusion of the perchlorate salt with potassium carbonate (Joan and Reedy, 1940). Repeated tests showed that both these methods are reliable. The conversion yield of chloride, measured gravimetrically and volumetrically (FID detector traces, ion chromatography and titration) is $100\pm 5\%$. The reproducibility of the isotopic analysis is $\pm 0.05\%$ for the chlorate (the same precision as for standard Cl isotopic analyses) and 0.1% for the perchlorate. Four samples of chlorate (different suppliers or batches) and three of perchlorate were analysed. In each sample of chlorate we found significant variations (up to 1%) between crystals, depending both on their shape and their size, the bigger the crystals the higher their $\delta^{37}\text{Cl}$ (Rayleigh fractionation during crystallisation?). Moreover, the $\delta^{37}\text{Cl}$ of the big crystals varied from -0.09 to $+0.45\%$, between samples. For perchlorate, the crystals were too small to allow analysis of the internal variability. However analysis of homogeneous solutions of perchlorate showed that each bag is characterised by a specific $\delta^{37}\text{Cl}$ value, namely 0.15 , 0.33 and 2.4% . These differences between the measured isotopic compositions of chlorine in the samples analysed, and the fact that they are different from the value expected of the feedstock chloride ($\sim -0.2\%$) suggest that the manufacturing process affects the isotopic composition of the product. Therefore, products from different plants and even different batches may have characteristically different isotopic compositions. However, from this limited survey it is impossible to make a more conclusive statement.

Coleman ML, McGenity TJ & Isaacs MCP, *Ninth Annual V. M. Goldschmidt Conference*, abstract #7253, (1999).

Eggenkamp HGM, *Ph. D Thesis Utrecht. Geol. Ultrai*, **116**, 150 pp, (1994).

Sister Joan M & Reedy JH, *Trans. Illinois State acad. Sci*, **33**, 123-125, (1940).

Vogel AL, *A textbook of quantitative inorganic analysis, theory and practice. 5th ed / revised by G. H. Jeffrey et al. Longmans, Green and Co. London*, 877 pp, (1989).

AI03 : MOam13 : F1 Radionuclides as Tracers of Atmospheric Fallout Enrichment Processes in Mountain Soils

Laurent Pourcelot (laurent.pourcelot@ipsn.fr)¹,

Didier Louvat (didier.louvat@ipsn.fr)¹,

François Gauthier-Lafaye
(gauthier@illite.u-strasbg.fr)²,

Mireille Del Nero

(mireille.delnero@ires.in2p3.fr)³ &

Peter Stille (pstile@illite.u-strasbg.fr)²

¹ Institut de Protection et de Sûreté Nucléaire (IPSN),
CEA Cadarache Bat 153, 13108 St Paul-lez-Durance,
France

² Ecole et Observatoire des Sciences de la Terre (EOST),
ULP/CNRS, UMR 7517, Centre de Géochimie de la
Surface, 1 rue Blessig, 67084 Strasbourg Cedex, France

³ Institut de Recherches Subatomiques,
ULP/CNRS/IN2P3, UMR 7500, 23 rue du Loess,
67037 Strasbourg Cedex 2, France, France

“Hot spot” soils were discovered in mountains of eastern part of France soon after the Chernobyl accident. These soils have a surface of only a few square meters but the ^{137}Cs concentration is hundred to thousand times higher than in common mountain soils. In order to elucidate and understand the processes of caesium enrichment, we used natural atmospheric fallouts as tracers. We also characterize the atmospheric deposition of metals in soil samples. Pasture grass, litter and soils were sampled on moraine located at 2200 m altitude in SE Alps, across a gradient of increasing ^{137}Cs activity. Gamma emitter activities show that in the “hot spot” soils the strongest ^{137}Cs activity occurred in the litter. Similar enrichments are also recorded for natural fallout radionuclides like ^{210}Pb (22.3 y) as well as ^7Be (54 d). Furthermore, direct deposition of natural nuclides on pasture grass is more important for “hot spot” soils than for less contaminated soils. In high altitude ecosystems the Chernobyl caesium fallout depositions occurred during snowfall. The wind accumulated the snow and, therefore, concentrated at these places the artificial radionuclides. Thus snow thickness and density as well as

^7Be activity in snow were measured on both “hot spot” and less contaminated soils. Data show that the strongest ^7Be snow accumulations are located on the “hot spot” soils with highest Cs concentrations. This strongly suggests that wind and morphology of the ecosystem strongly controlled the enrichment process of Cs fallout at the time of Chernobyl accident. This is also supported by other geochemical data of the soils which indicate that “hot spot” soils are widely enriched in anthropogenic metals of atmospheric origin (Pb, Sb, Zn, Cu, Ni). Thus despite dispersion processes occurring in the air, atmospheric pollutants may be strongly concentrated on soils when fallouts occurred in such mountain environments. After snow-break, radionuclides have been remobilized by meteoric waters. Organic matter, mineral phases and pH/Eh of the soil and soil solution controlled their enrichment in the “hot spots” and favoured the scavenging of Cs and other radionuclides in the soils.

Froideval et al., *J. Conf Abs* **6**, 39 (2001).

Aubert et al., *J. Conf. Abs.* **6**, 39 (2001).

