

## Reactivity of waste generated during lead recycling: An integrated study

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Available online 18 April 2006

### Abstract

Lead consumption in Europe is 2.054 M tonnes/year, more than 70% of which is produced by recycling and, more specifically, the recycling of car batteries. This industry is jeopardised by the method employed so far, recycling by alkaline fusion, because the treatment produces 200,000 tonnes of toxic and unstable slag. The study presented here attempts to clarify the approach and the combined tools employed (mineralogy, chemistry, leaching, thermodynamics), to construct a coherent physicochemical model of slag behaviour. The model was then used to carry out sensitivity analyses with various landfill scenarios, and to propose adjustments to the process to recover the residual heavy metals and to upgrade as secondary raw products the co-products generated by the inerting of the slag.

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**Keywords:** Secondary lead; Refining; Alkaline slag; Mineralogy; Chemistry; Thermodynamics; Geochemical modelling

### 1. Introduction

Lead consumption in Europe is 2.054 M tonnes/year, more than 70% of which is produced by recycling and, more specifically, the recycling of car batteries. Yet the equilibrium of this industry is in jeopardy for two reasons: on the one hand, the source and the cost of the recycled lead mainly supplied by the battery market fluctuates considerably, and on the other hand, the method used so far is recycling by alkaline fusion. Each year the treatment produces 200,000 tonnes of toxic and unstable slag, as well as 280,000 tonnes of sludge from the neutralisation of the sulphuric acid present in the batteries. An evaluation of the process reveals the negative impact on the environment. With the regulations stiffening in Europe, the possibility of landfilling the waste is diminishing, despite the lack of an economic alternative to lead batteries. It is therefore important to accurately investigate the nature of the alkaline slag, to evaluate its reactivity, and to propose alternative solutions to landfilling, while ensuring the security of the industries that still recycle lead in Europe.

The ‘SCORP’ (Pb SCORia) study described in this article attempts to clarify the approach and the combined tools

employed (mineralogy, chemistry, leaching, thermodynamics), to construct a coherent physicochemical model of slag behaviour. The model was then used to carry out sensitivity analyses with various landfill scenarios, and to propose adjustments to the process to recover the residual heavy metals and to upgrade the co-products generated by the inerting of the slag.

### 2. Material and methods

#### 2.1. Slag production

The thermal refining of lead takes place in the liquid phase; the lead must be molten at temperatures bounded by its melting point (327 °C) and its boiling point (650 °C). During molten lead refining, reagents are selectively added to remove other metals (Cu, Sn, As, Ag, etc.) [1]. The battery lead recycling process essentially involves the addition of caustic soda (NaOH) and sodium nitrate (NaNO<sub>3</sub>) to trap the metals in the form of oxides (arsenites, antimonites and stannites) that are collected on the surface of the molten lead bath. The reduction of the residual sulphates resulting from the battery electrolyte then produces sulphides (NaFeS<sub>2</sub>, FeS, FeS<sub>2</sub>, Na<sub>2</sub>S). Carbon in the form of coke can be added to the molten bath to control the redox couple. The slag produced is cooled in an aerated box allowing complete maturation prior to being sent to a landfill facility.

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## 2.2. Samples

Three types of alkaline slag were investigated: (i) fresh (FPS—Freshly Produced Slag) resulting directly from the recycled lead production process; (ii) after an accelerated maturation cycle (to increase the kinetics of the sulphur oxidation) under airflow in vibrating screens until its disintegration into a black powder (1WAS—1 Week Aged Slag); (iii) after 5 years exposure to climatic conditions in a lysimetric box (5YWS—5 Years Weathered Slag).

The FPS slag was sampled from 5 to 20 cm slag blocks taken at random. Due to the high reactivity of the slag with the atmosphere, the blocks investigated were produced by breaking up larger blocks, in order to sample the least oxidised material. The 1WAS slag was used for up-flow percolation tests and the construction of a lysimetric box by the CERED-SITA laboratory as part of the ADEME Research Project on the Ecocompatibility of Waste in 1999 [2]. Data are given below. After 5 years of exposure to weathering, the 5YWS slag was sampled by auger for mineralogical analysis and element mobility analysis.

## 2.3. Leaching tests

Several tests were conducted on FPS slag to determine its reactivity and to compare the contents of the eluates with the reference values of European Council Directive 1999/31/EC of 26 April 1999 on the landfilling of hazardous waste. In addition to the EN 12457-2 tests (batch tests) and TS 14405 (up-flow percolation [2]), sensitivity tests to forced variations in intensive parameters were carried out by the addition of acid (pH 4, 7, 10) or oxidant ( $H_2O_2$ ), or by carbonation, in order to assess the response of the slag to the physicochemical variations imposed on the environment, for various scenarios.

## 2.4. Analytical methods

The analytical protocols were adjusted to preserve the samples, due to the extreme reactivity of the FPS (oxidation): use of inert gas, minimum-handling time, storage of the samples in closed containers. Due to the probable presence of sulphur

bearing colloids, the water produced by the different tests was subjected to analysis, with or without filtration after settling, and ultra-filtration. The samples were analysed by X-ray diffraction, electron microscope and electronic microprobe.

## 3. Results

### 3.1. Mineralogy and solid chemistry

The particle size distribution of the FPS slag was very heterogeneous, ranging from metre sized blocks (content of a crucible) to dust. The blocks mainly consisted of oriented elongate crystals of sulphides. The casting bottom often displayed a film of lead metal. The next higher zone (10–20 cm) contained droplets of lead metal. The superficial part of the block displayed the appearance of a frozen border with a finer particle size distribution of the sulphides and the presence of vacuoles. The exothermic oxidation is rapid, and the slag disintegrates into a fine blackish dust. This reactivity may be violent: spontaneous combustion (highly exothermic reaction with oxidation of iron) raising the samples to high temperatures were observed in the cooling rooms, and also during grinding of the samples. The major phases identified correspond to an alkaline iron sulphide ( $NaFeS_2$ ) and its hydrated equivalent  $NaFeS_2 \cdot 2H_2O$  already identified in the natural environment and known as Erdite. After intense leaching, the weathered slag (5YWS) assumed the form of a hydromorphic dark red sludge composed of iron hydroxides, containing residual lead, vitreous and metallic slag and residual minerals like Valentinite  $Sb_2O_3$  (Table 1). The relative mobility associated with leaching of the elements can be identified (Fig. 1) by Grant's approach [3]. The chemistry has changed radically with the departure of the extremely soluble elements (Na, S, Cu), then moderately soluble elements (Fe, Zn, Mn, Ca, K), and the preservation of the insoluble elements (Al, Mg, Pb, Ti, Si, Cd, Ni, Sb). The latter are controlled by the vitreous slag, and by certain minerals such as magnetite for Ni, and valentinite for Sb. Based on this representation, it is also possible to evaluate a weight loss of 60% of the dried product after leaching that is consistent with the volume variation measured on the lysimeter (70%).

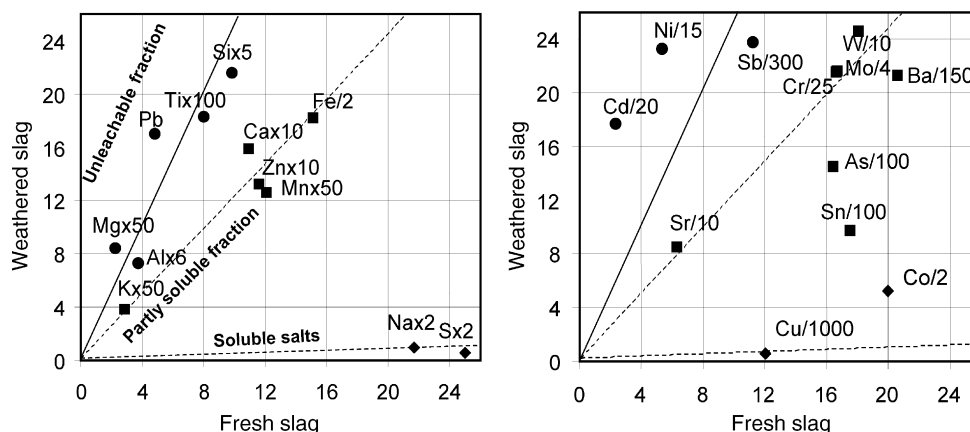


Fig. 1. Grant's isocon diagram [3] highlighting the relative element mobility, comparison between fresh and weathered slag. Key: dots (●) unleachable elements distributed with a slope of 8 per 20, squares (■) moderately leachable elements, diamonds (◆) extremely leachable elements (salts).

Table 1  
Fresh and weathered slag: synthesis of XRD, SEM and electronic microprobe data

Mineral family and name	Structural formula	Freshly Produced Slag (FPS)	5 Years Weathered Slag (5YWS)
<b>Sulphurs</b>			
Sodium iron sulphides	NaFeS <sub>2</sub>	Abundant	
Erdite	NaFeS <sub>2</sub> ·2H <sub>2</sub> O	Abundant	
Galena	PbS	Probable	
Pyrrhotite	FeS	Probable	
Chalcopyrite	CuFeS <sub>2</sub>	Probable	
Pyrite	FeS <sub>2</sub>	Probable	
<b>Tectosilicate</b>			
Quartz	SiO <sub>2</sub>		Traces
<b>Oxides</b>			
Magnetite	Fe <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> O <sub>4</sub>	Present	Weak
Wüstite	FeO	Present	Weak
Valentinite	Sb <sub>2</sub> O <sub>3</sub>	Traces	Weak
<b>Sulphate</b>			
Thenardite	Na <sub>2</sub> SO <sub>4</sub>	Traces to present	
<b>Carbonate</b>			
Cerussite	PbCO <sub>3</sub>	Traces	Traces
<b>Elements</b>			
Iron	Fe, Sn (traces)	Traces	
Lead	Pb <sup>o</sup>	Traces	Present
Graphitic carbon	C		Weak
<b>Alloys</b>			
Metal bearing slag	Pb, Sb	Traces	Weak
Vitreous silicate-bearing slag	Fe, Pb, Cu, Zn, Sn, Co, Cr, W, Ni	Present	Present
Amorphous phases	Si, Pb, Ca, Al, . . .	Present	Present
		Abundant	Abundant (iron hydroxides)

Abundance indexes: abundant > present > traces > weak > probable (not identified with satisfactory accuracy).

### 3.2. Leaching test

The application of the batch leaching test on FPS according to standard XP 30-402-2 (transposed from European standard EN 12457-2) required an adjustment of the filtration due to the production of colloids. Centrifugation was thus used to obtain a limpid solution that could be analysed, because the traditional filtration protocol (0.45 µm) is not very efficient and crude solution has a sedimentation time span that is too long.

The contents of the leachates were close to or above the limit values – thresholds – of the French class 1 Decree for As, Mo, Sb, Se and for the soluble fraction. The pH obtained was very close to the authorised maximum of 13. Emanations of hydrogen sulphide H<sub>2</sub>S were observed during the opening of the reactors.

Sensitivity tests to pH variations, and to oxidation, showed that the reactivity of the slag is highly dependent on the physico-chemical conditions of the environment (Fig. 2). The drop in pH, controlled by the addition of HCl, reduces the solubility of most of the heavy metals. On the contrary, it increases the solubility of the major species (Fe, Na, Mn). Oxidation in basic medium (pH ≈ 10) increases the solubility of the transition metals (Cd, Pb, Zn) and the concentration of the Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> couple. In all cases, the resulting variations cause overruns of one or the other of the thresholds. Uncoupling the Na<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> ratio from one test to another (sensitivity to acidity or to oxidation) appears to be associated with the formation of S<sup>o</sup> (see Fig. 2, B column Sred) trapped in the residual solid in acidic medium.

The slag maturation tests also revealed its sensitivity to gaseous inputs. Leaching with the addition of pure CO<sub>2</sub> causes a substantial drop in pH (≈7), and the release of H<sub>2</sub>S, mainly accompanied by the dissolution of Na, Ba, Mo, Sb and Se. Values for the latter three elements exceed the thresholds. Oxidation under airflow progressively enriched with oxygen is accompanied by a brown colour indicating the oxidation of some of the iron, and the significant dissolution of Na, Sn, As, Pb, Sb and Se. Values of the latter four elements exceed the thresholds.

Moreover, the up-flow percolation test on an oxidised slag (1WAS) revealed a two-step leaching (Fig. 3): (i) complete leaching of a salt, thenardite [Na<sub>2</sub>SO<sub>4</sub>], with a chemical system controlled by the salinity of the medium and (ii) then above a L/S ratio of 3.7, initiation of a second system less dependent on salinity.

### 3.3. Thermodynamics of NaFeS<sub>2</sub>

Due to the lack of thermodynamic data in the literature for anhydrous and hydrated sodium iron sulphides that are abundant in slag (FPS, Table 1), an approach had to be developed comprising: (i) the estimation of  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$  and  $S^\circ$  for the anhydrous mineral [NaFeS<sub>2</sub>] using an ideal solid solution model with three poles (Pyrite [FeS<sub>2</sub>], Pyrrhotite [FeS] and sodium sulphide [Na<sub>2</sub>S]); (ii) measurement at 25 °C of the solubility constant of Erdite [NaFeS<sub>2</sub>·2H<sub>2</sub>O] produced by contact of NaFeS<sub>2</sub> with

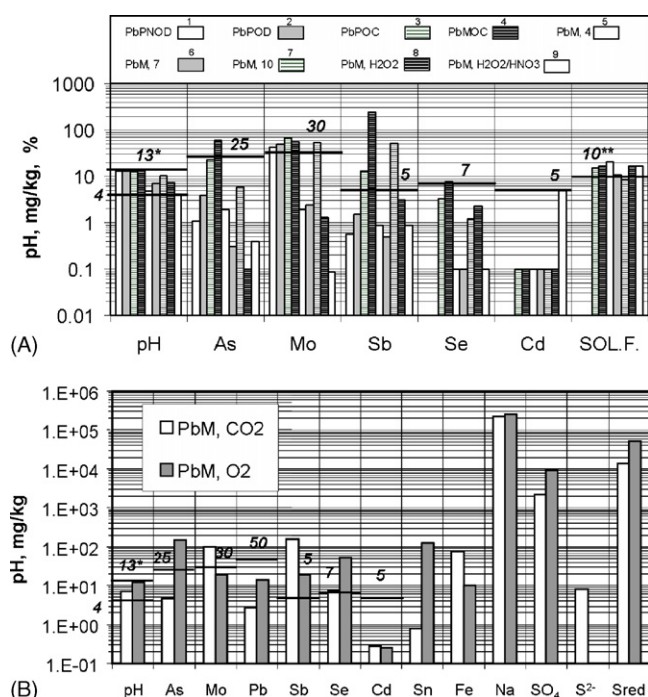
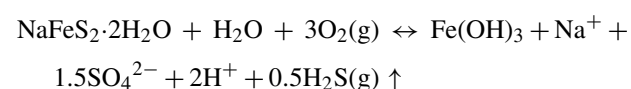
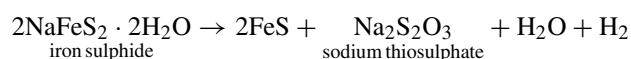
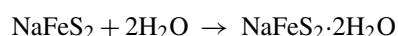


Fig. 2. Leaching test results, log scale, L/S = 10: (A) PbPNOD, PbPOD, PbPOC, PbMOC (standard prEN 12457-2); PbM 4, PbM 7, PbM 10, PbM H<sub>2</sub>O<sub>2</sub>, PbMH<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>; (B) PbM CO<sub>2</sub>, PbM O<sub>2</sub> (sensitivity tests). Keys: unoxidised slag and settled leachant (PbPNOD), oxidised slag and settled leachant (PbPOD); oxidised slag (lead paste type) and centrifuged leachant (PbPOC); oxidised slag (lead metal type) and settled leachant (PbMOC); sensitivity tests to different pH with HCl (PbM 4–10); sensitivity tests with different reagents (H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> + HNO<sub>3</sub>, CO<sub>2</sub>, O<sub>2</sub>), PbM H<sub>2</sub>O<sub>2</sub> to PbM O<sub>2</sub>. In italics, compliance values from Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC and French regulation\*. 1 to 9 lecture order of the caption. SOL. F., solid fraction.

water; (iii) comparison of the resulting hydration energy with the values in the literature. The basic data necessary for these calculations are given in Table 2.

The instability of Erdite observed is clearly illustrated in the pH–Eh phase diagram (Fig. 4, calculated for the concentrations measured in the experiment, Table 2). The Erdite produced by the hydration of NaFeS<sub>2</sub>, which is a very fast reaction, is soon completely destabilised to Pyrrhotite or Pyrite, or Magnetite [Fe<sup>2+</sup>Fe<sub>2</sub><sup>2+</sup>O<sub>4</sub>], depending on the relative concentrations of Fe, S, and Na, O<sub>2</sub>, H<sub>2</sub>O of the system. Thus to illustrate this instability, a reaction path can be suggested, i.e. Erdite NaFeS<sub>2</sub>·2H<sub>2</sub>O can be destabilised to yield sulphides, sulphites, or sulphates, depending on the redox conditions:



### 3.4. Models of performance assessment

In France, the landfill concept for special industrial waste (having a very high pollutant potential) relies on the double safety provided by: (i) the containment of the waste and (ii) its stabilisation. If the waste is only contained, its pollutant potential is preserved, but remains a potential threat in the case of containment failure. To avoid such risks, a solidification-stabilisation procedure can be adopted. Commonly, this consists in adding a binder to harden and inertise the waste by the precipitation of pollutant-trapping mineral phases. Unfortunately in our case, the waste cannot be solidified because of the extremely high reactivity of the fresh slag and the huge content of strongly soluble salts in the oxidised slag.

Due to the difficulty of approaching high ionic strengths  $I$  (in the conventional model  $I < 1 \text{ mol/l}$ ) with currently available computer codes, two types of scenario were considered:

- Type A scenarios: landfilling is assumed for which the slag has been stored oxidised with its original salinity (scenarios A1, A2, A3, Table 3).
- Type B scenarios: landfilling is assumed for which the relatively unoxidised slag has been stored after leaching of most of the salts (scenarios B1, B2, B3, B4).

In the first series of scenarios, it is proposed to use the semi-analytical computer code MISP [6] to simulate the potential impact on an aquifer of leachates emitted by the saline slag in a landfill scenario, with characteristics selected based on scenarios used for defining the acceptance criteria for landfilling of waste (Annex II of Directive 1999/31/EC).

These simplified simulations help to illustrate the fact that without stabilisation, the anticipated reduction for extremely reactive salts (like the sodium sulphate) is slight given the high concentrations expected from the up-flow percolation tests. It is therefore clear that without stabilisation, this raw waste placed in a class 1 landfill represents a long-term threat to groundwater quality, as implied by the results of the MISP software (Fig. 5).

The simulations made using more sophisticated computer codes PHREEQC [8], PHAST [9], on unoxidised slag stored after the departure of most of the salts, requires the establishment of a typical source term mineralogy. This was established from the mineralogy observed and from realistic assumptions, concerning the potential minerals based on the knowledge of the pyrometallurgical processes (i.e. Arsenolite As<sub>2</sub>O<sub>3</sub>), and concerning the secondary minerals likely to precipitate. Four scenarios were analysed for this sensitivity analysis (Fig. 6).

The calculations performed with the scenarios help to identify the key parameters influencing the behaviour of the waste over time:

- (1) The partial pressure of hydrogen sulphide H<sub>2</sub>S, controlled by permitting or preventing the degassing of this compound for equilibrium with the atmosphere, very strongly influences the future of the waste. In scenarios B1 and B3 (H<sub>2</sub>S degassing) the sulphides leave the solution, causing dissolution of all Erdite, whereas in scenarios B2 and B4, the

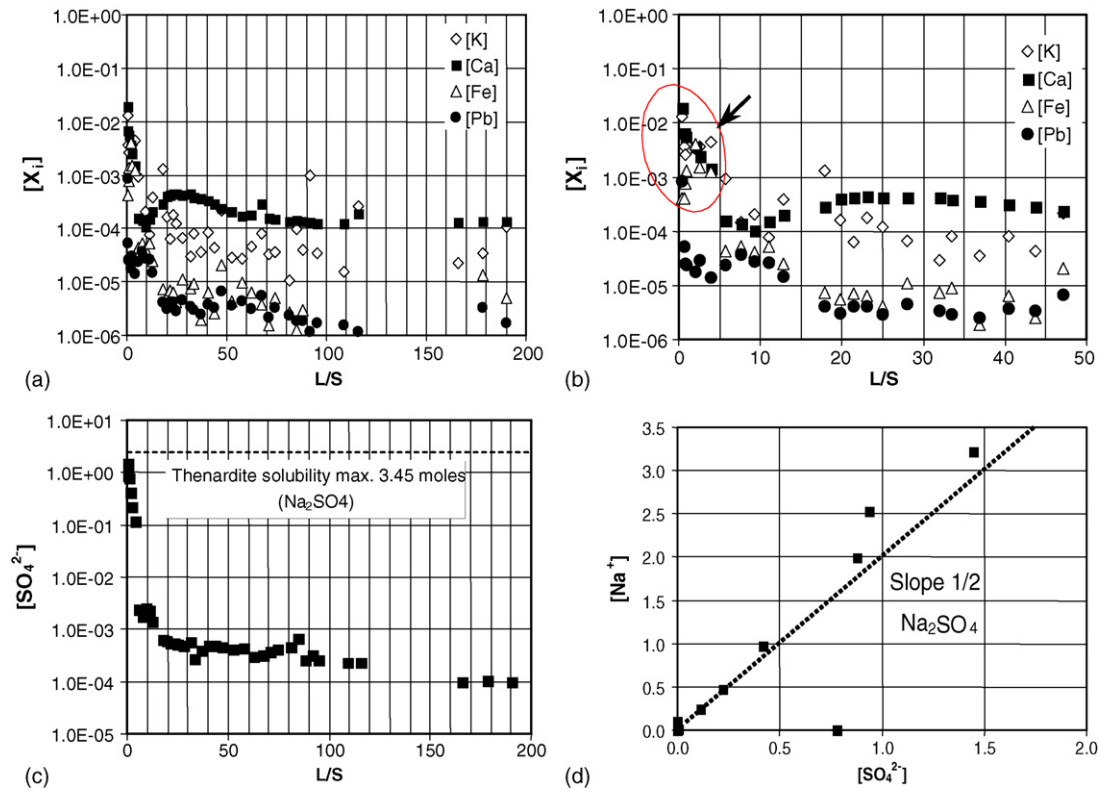


Fig. 3. Up-flow percolation test (under specified conditions) on oxidised slag: K, Ca, Fe, Pb, concentrations [ ] in mol/kgw vs. L/S, (a) in the range 0–200 L/kg, (b) in the range 0–50 L/kg, (c)  $\text{SO}_4^{2-}$  concentrations (mol/kgw) vs. L/S in the range 0–200 L/kg, (d) correlation between  $\text{SO}_4^{2-}$  and Na from a L/S from 0.01 to 1.5 L/kg (raw data from [2]).

Table 2  
Data used to calculate thermodynamic constants for  $\text{NaFeS}_2$  and Erdite

Calculation made with TR98 <sup>a</sup> base								
	pH	Eh (mV)	$\log(\text{Na}^+)$	$\log \text{Fe}(\text{OH})_3^-$	$\log(\text{HS}^-)$	$\log(\text{O}_2^0)$	$\log(\text{H}_2\text{O})$	$\log Q$
Part (A)								
Essay 1	11.81	−532	−1.64	−4.03	−2.32	−76.75	−3.0E−4	−53.1 ± 0.1
Essay 2	11.83	−533	−1.66	−4.33	−2.33	−76.76	−3.0E−4	−53.5 ± 0.1
Essay 3	11.82	−532	−1.63	−4.55	−2.34	−76.71	−3.0E−4	−53.7 ± 0.1
Compound	Dissolution reaction					$\Delta G_f^\circ$ (J/mol)	$\log K$	
Part (B)								
$\text{Fe}(\text{OH})_2$	$\text{Fe}(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$					−486500	13.74	
$\text{Fe}(\text{OH})_3$	$\text{Fe}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$					−696500	5.49	
$\text{FeSO}_4$	$\text{FeSO}_4 \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}$					−820800	2.41	
Goethite	$\text{FeOOH} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$					−488510	0.37	
Magnetite	$\text{Fe}_3\text{O}_4 + 8\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{H}_2\text{O}$					−1014930	9.97	
Pyrite	$\text{FeS}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 1.75\text{HS}^- + 0.25\text{SO}_4^{2-} + 0.25\text{H}^+$					−160218 <sup>b</sup>	−24.91	
Pyrrhotite	$\text{FeS} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{HS}^-$					−100767 <sup>b</sup>	−3.93	
	$\Delta G_f^\circ$ (J/mol)	$\Delta H_f^\circ$ (J/mol)	$S^\circ$ (J/mol K)	$\log K$				
Part (C)								
$\text{NaFeS}_2$	−310500	−319100	113.9	−18.4 <sup>c</sup>				
Erdite ( $\text{NaFeS}_2 \cdot \text{H}_2\text{O}$ )	−819200	−941600	198.6	−24.4 <sup>d</sup>				
Hydration water	−254300	−311200	42.4					

(A) Analytical characteristics of equilibrated solution with erdite and speciation calculated with Phreeqc code. (B) Stoichiometric equation used for constant computation and phase diagram construction. (C) Thermodynamic constant for  $\text{NaFeS}_2$ , Erdite and hydration water ( $\cdot\text{H}_2\text{O}$ ).

<sup>a</sup> TR98 (from [4], and [5]).

<sup>b</sup> Data same as slop98.dat.

<sup>c</sup>  $\text{NaFeS}_2 + 0.5 \text{H}_2\text{O} + \text{H}^+ \leftrightarrow \text{Na}^+ + \text{Fe}^{2+} + 2\text{HS}^- + 0.25\text{O}_2^0$ .

<sup>d</sup>  $\text{NaFeS}_2 \cdot 2\text{H}_2\text{O} + \text{H}^+ \leftrightarrow \text{Na}^+ + \text{Fe}^{2+} + 2\text{HS}^- + 1.5\text{H}_2\text{O} + 0.25\text{O}_2^0$ .

Table 3  
Input parameters used in scenarios A [7]

	Waste cell dimensions in m length × width × height	Other parameters	
Scenario A1	50 × 50 × 20	Compacted clay liner	Thickness 5 m, porosity 30%, permeability 10 <sup>-9</sup> m/s, longitudinal dispersion coefficient 0.5 m
Scenario A2	50 × 50 × 5	Aquifer	Permeability 10 <sup>-4</sup> m/s, hydraulic gradient 0.7%, porosity 25%, dispersivities, longitudinal 10 m, horizontal-transverse 3 m, vertical-transverse 1 m
Scenario A3	50 × 10 × 20		

In bold the parameter which varies with the scenario.

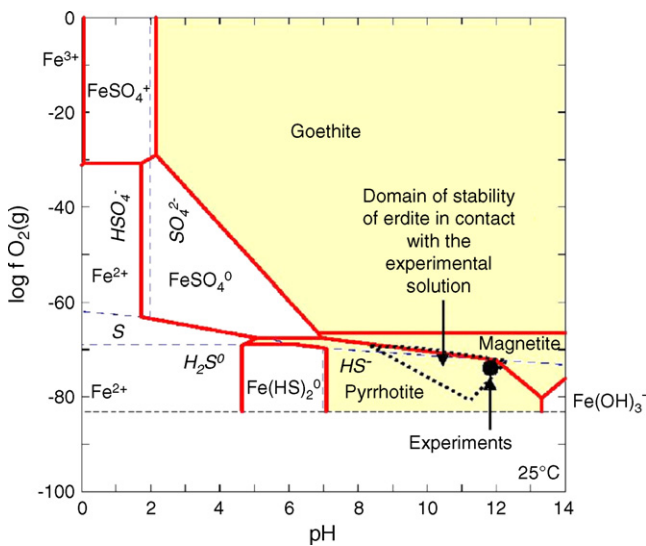


Fig. 4. Phase diagram pH-f(O<sub>2</sub>) for Na-Fe-S-H<sub>2</sub>O system for Goethite, Pyrrhotite, Magnetite, Erdite. Element concentrations are those of experiments performed for the solubility constant measurement carried out for Erdite. Shaded area corresponds to solid phases, solid lines to iron species.

sulphides remain in solution and Erdite largely remains in the system (thereby maintaining the potentially pollutant nature of the waste over the longer term). Moreover, in scenarios B1 and B3 (H<sub>2</sub>S degassing) secondary phases containing lead precipitate, thus limiting the leaching of this

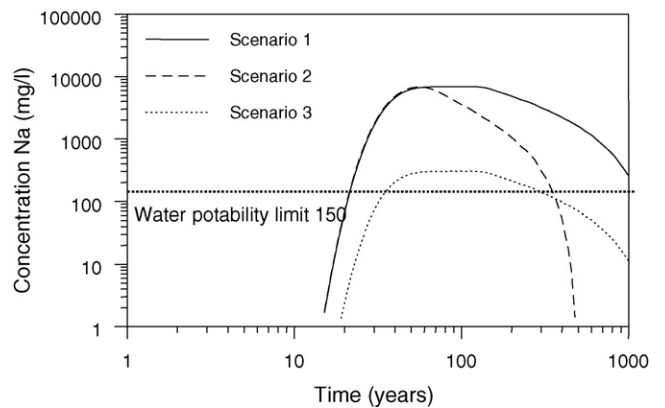


Fig. 5. Change in Na concentration with time elapsed, 100 m away from the source, according to scenarios A1, 2, 3 (results from MISP simulations).

metal. By contrast, in scenarios B2 and B4, the aqueous lead forms complexes with the sulphides in solution, favouring the leaching of lead metal. Fig. 7 shows indeed that when H<sub>2</sub>S can degas (scenario B1, p<sub>H<sub>2</sub>S</sub> = 10<sup>-9.7</sup> bars), approximately 50% of the dissolved lead (Pb<sup>2+</sup>) is available for mineral precipitation. Conversely, when H<sub>2</sub>S cannot degas (scenario B2, equivalent p<sub>H<sub>2</sub>S</sub> = 10<sup>-3</sup> bars), it complexes with almost the totality of dissolved lead. This leads to total lead concentrations in scenario B1 that are 1000 times lower than in scenario B2, but with Pb<sup>2+</sup> concentrations that are 20

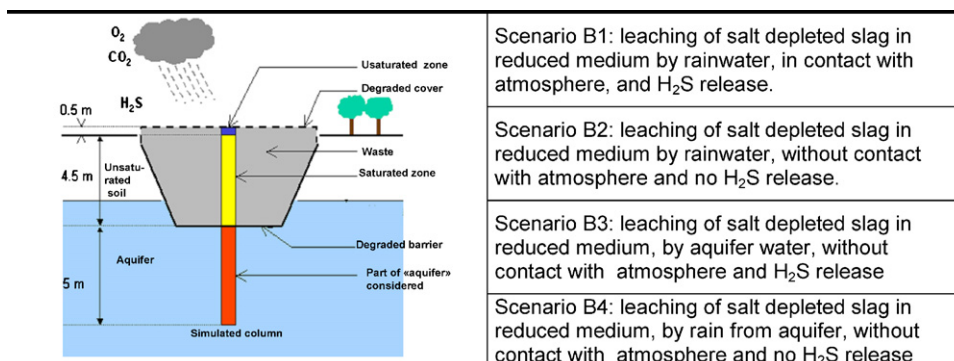


Fig. 6. Assessment modelling, schema of scenarios B.

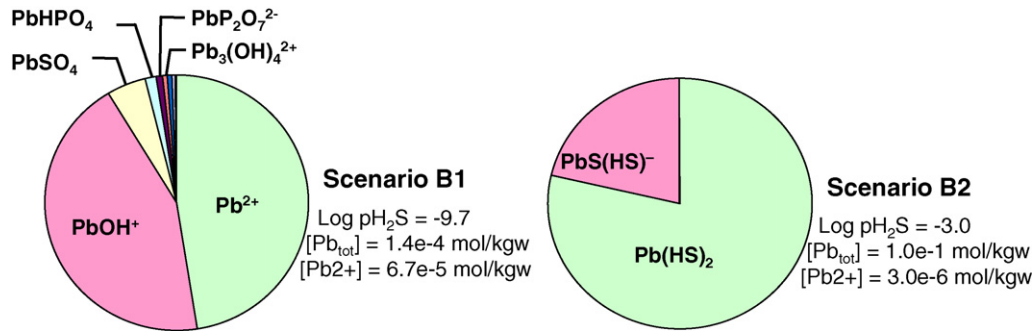


Fig. 7. Aqueous speciation of dissolved lead according to scenarios B1 and B2 (see text for details).

- times higher (with possible equilibrium with mineral phases such as Anglesite or Cerussite) compared to scenario B2.
- (2) The partial pressures of the other gases (oxygen and carbon dioxide) can be fixed in the form of an imposed mobility for  $O_2$  and  $CO_2$  in the upper portion of the system (scenario B1). The zone concerned simulates an unsaturated zone where the gas exchanges are substantial, causing very different chemical behaviour from that simulated at greater depth, but which gradually gains the rest of the waste (Fig. 8).
  - (3) The chemical composition of the seepage water also influences the evolution of the waste: contrary to scenario B1, scenario B3 predicts the formation of siderite, since the aquifer water injected into the waste contains ten times more carbonate than the rainwater.

An example of evolution for the system in the case of scenario B1 is shown on Fig. 8, in terms of lead and sulphate concentrations as a function of depth, at various times. Three steps can be distinguished. At early times after the beginning of the simulation (first 20–30 years), leaching of the very soluble salts ( $Na_2SO_4$ ) is illustrated by the behaviour of the dissolved sulphate. Next, the concentrations of both sulphate and lead are controlled by equilibrium with Anglesite ( $PbSO_4$ ). This mineralogical control is progressively replaced by other ones as Anglesite is depleted: Barite ( $BaSO_4$ ) for sulphate and Cerussite ( $PbCO_3$ ) for lead. This mineralogical control of dissolved lead

may contribute to the surface passivation phenomenon, which limits leaching of lead. This explains that metal lead remains in the waste as has been observed on samples of slag collected after 5 year duration in situ experiments (5YWS).

#### 4. Summary and perspectives

The analysis of alkaline slag from the second fusion of lead demonstrates the reactivity of this waste, which is a Hazardous Industrial Waste that, according to French Decree 2002-540 of 18 April 2002 relative to the classification of waste, could, depending on the exposure conditions, display warming properties (criterion H3-A), toxicity (criterion H6), corrosiveness (criterion H8), acid production (criterion H12) properties making it sensitive to leaching (criterion H13), and evident ecotoxicity (H14). Most of the criteria checked by this study demonstrate that this waste is a Special Industrial Waste and must be treated as such.

The results obtained show that the high sensitivity of the waste to the physicochemical conditions of the environment derives from the presence of sulphur, and from its oxidation state, which governs its reactivity: spontaneous combustion,  $H_2S$  emanations, production of highly soluble alkaline sulphates, solubilisation of metals by complexation, ionic strength also having a probable role in this solubilisation. Only the elimination of the sulphur could conceivably allow disposal

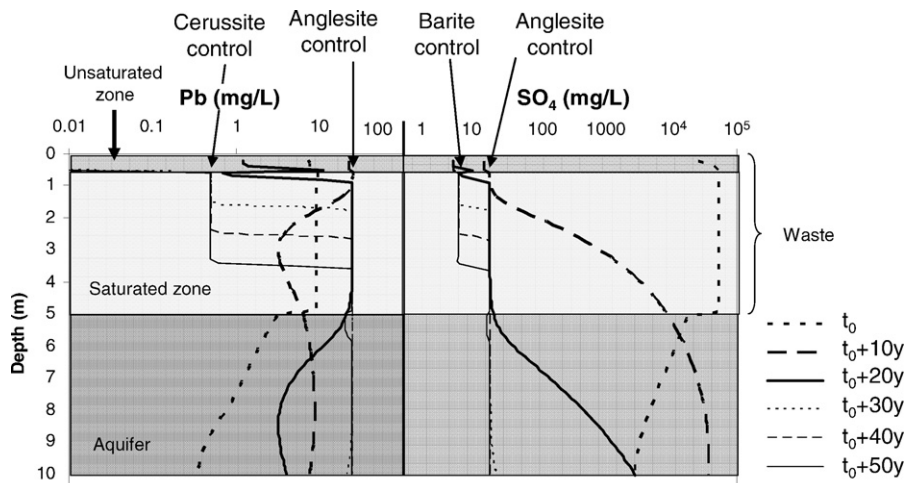


Fig. 8. Simulated dissolved lead and sulphate in depth profiles, at various times and for scenario B1, illustrating successive mineralogical controls of these elements.

in a Waste Landfill guaranteeing reasonable safety. Only after a stage of stabilisation and solidification can this waste be landfilled with an optimal degree of safety.

These results all tend towards a single conclusion: alkaline slag from the second fusion of lead cannot be landfilled as such, neither in a contained environment (danger of gaseous emanations in case of possible oxidation, reactivity), nor after forced oxidation (solubility of secondary salts), nor can it be stabilised due to the extent of the soluble fraction of the waste ( $\approx 70$  vol.%). It therefore appears necessary to supplement this study with a search for alternatives aimed to use this waste as a secondary raw material, while decreasing its pollutant potential. Three different alternatives are considered hereafter.

#### 4.1. Use of the waste as a reducing reactant

Freshly produced alkaline slag displays high reducing power that could be used to generate sulphide from the heavy metals present in certain leachates, like those produced by the surface treatment of metals before electroplating, or to stabilise mercury bearing effluents. Yet this first alternative is not worth investigating because it will remove little, if any, of the potentially pollutant character of this waste, i.e. reactivity and solubility.

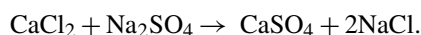
#### 4.2. Production of sulphuric acid from the waste

The combustion of the waste in a fluidised bed microfurnace could decrease the leachable potential of the waste. Since this consists mainly of highly reactive  $\text{NaFeS}_2$ , the energy expenditure would be very low, with the possibility of spontaneous combustion maintained by the enthalpy of the oxidation reaction. Part of the sulphur could be recovered in the form of  $\text{SO}_2$  and then  $\text{SO}_3$  (catalytic reaction) to produce sulphuric acid. However, a part of the metals present in the waste will be volatilised (As, Sb), and a gas treatment unit would be necessary to recover the metals in the form of potentially upgradeable oxides. This costly solution in terms of gas treatment would demand greater scrutiny. One cannot discount the possibility of the fusion of residual slag (rich in Na) that could hamper the process.

#### 4.3. Combined use with other waste types having complementary properties

A third theoretically more encouraging alternative can be discussed that could decrease the pollutant potential of two industry by-products by combining two waste types. To implement the process selected, it is planned to 'mature' the slag under an air stream (fluidised bed) to oxidise the sulphur and produce thenardite [ $\text{Na}_2\text{SO}_4$ ]. This highly soluble sulphate could

be leached to produce an effluent. Separated from the rest of the waste, this effluent would abandon, in the remaining solid, part of the heavy metals trapped in the slag, for instance in the residual iron hydro-hydroxides and lead metal ( $\approx 15\%$ ). At this stage, the lead metal could be extracted by a physical process exploiting its high density. Various theoretical alternatives have been considered for stabilising the thenardite. Only the use of calcium chloride (waste from bicarbonate production) seems to be promising, with a negative free energy for the reaction:



The analysis of this alternative would require further investigation. However, the precipitation of  $\text{CaSO}_4$  and of  $\text{NaCl}$  could set the stage for the use of these two salts as secondary raw materials.

#### Acknowledgements

The authors are grateful to Rowena Stead for translating the original French text and to the anonymous reviewer for their detailed review and constructive comments.

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