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The influence of reducing conditions on the dissolution of a Mn-rich slag from pyrometallurgical recycling of alkaline batteries

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ABSTRACT

The redox potential (Eh) is a key parameter for controlling the release of elements from solid materials. Nevertheless, this parameter is seldom taken into account during risk assessment studies within any regulatory framework. We studied the incidence of redox changes to the solid materials using two batch procedures: i) a gradient of redox conditions obtained using sodium ascorbate solutions at various concentrations; ii) N_2 bubbling in water. These experiments were performed on two Mn-rich slag samples coming from a pyrometallurgical plant that recycles alkaline batteries. Both samples differed slightly in their chemical composition and solid characterization (*i.e.* presence of Mn oxide) and presented different behaviours. The present study focused on the release of the main slag elements (*i.e.* Mn and Si) chosen as indicators of the dissolution of primary silicate phases. Solid phase analyses (SEM-EDS and XRD) were coupled with the monitoring of elements in leachates in order to understand their behaviour and the mechanisms involved. The results indicated that the solid composition plays an important role in the release mechanisms. The presence of Mn oxide enhanced the mobilization of Mn in the greatest reducing conditions (−320 ± 5 mV/SHE), to the extent that 42% of the total Mn was leached. This demonstrated the significance in studying the solid phases (using SEM-EDS and XRD) before and after any leaching experiment. From a laboratory practice point of view, it was easier to use sodium ascorbate and allowed, in our case, greater reducing conditions to be reached.

1. Introduction

Slags constitute a by-product from pyrometallurgy arising from (i) the concentration of impurities in molten metals and (ii) the oxidation of metals on their contact surface by air. The liquid hot slags are separated from the molten metals, and then cooled to ambient temperature. Significant volumes of slags are produced yearly throughout the world, either from ferrous or non-ferrous metallurgy production. In 2008, the world production of ferrous slag was approximately 240–290 Mt and the output of steel slag represented about 115–170 Mt (data from http://minerals.usgs.gov/minerals/pubs/commodity/iron_&_steel_slag/mcs-2009-fesla.pdf).

Slags are either dumped or reused as a secondary material in order to preserve natural resources and their after-life is an important economical and ecological concern. In Europe, around 50% of steel slags are reused in road construction and only 11% are dumped (http://www.ctpl.info). In all cases, environmental safety has to be investigated because of the potential mobility of their constituents such as metallic elements. To assess the risk of contamination, various standardized leaching procedures are available depending on the country's legislation, the origin of solid materials and the way they will be reused. These tests allow the influence of a parameter in controlled conditions to be easily studied, however the results are often difficult to translate to "in-situ" environmental conditions. Most of them are performed with high-purity water (*i.e.* EN 12457-1, 2002). Some are carried out by studying the effect of pH conditions (*i.e.* XP CEN/TS 14997, 2006) but none takes into account the influence of the redox potential (Eh) on the release of elements, despite its role in the control of the speciation and/or the mobility of elements. Nevertheless, the Dutch standard NVN 7348 (Draft) (1994) proposed to determine the redox properties of a material by evaluating its reducing capacity using a batch leaching experiment and monitoring the redox potential, such as that used by Mizutani et al. (2000) on municipal solid waste incineration residues. Redox potential is now recognized to be, like pH, a key factor in element release mechanisms (Fällman and Aurell, 1996; Quevauviller et al., 1996; van der Sloot et al., 1996; Wahlström, 1996; Cappuyns and Swennen, 2008; Davranche and Bollinger, 2000; Fällman, 2000). Nevertheless, during environmental risk assessments of slags, its influence has not been studied until now.

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It is difficult to impose and control reducing conditions. The influence of the redox potential on element release has been studied from soil suspensions, using reducing reagents such as sodium ascorbate (Davranche and Bollinger, 2000; Chatain et al., 2005; Pareuil et al., 2008). Redox conditions were also modified and studied with O_2 and/or N_2 bubbling (Patrick et al., 1973; Charlatchka and Cambier, 2000) to influence the oxic or anoxic conditions. When redox conditions are studied, in soil samples for example, microorganisms can play an important role (Quantin et al., 2001) but they are more difficult to control.

The present study focused on an Mn-rich slag originating from a pyrometallurgical process that recycles alkaline batteries to produce ferromanganese alloy. Each year, this plant produced around 2500 t of Mn-rich slag. The two representative samples studied here differed in their chemical and mineralogical composition. It is most likely that different cooling conditions led to the crystallization of different mineral phases. For example, the presence of manganosite (MnO) was observed in only one of the two samples. In addition, their manganese content varied from 380 to 500 g/kg. They were submitted to various redox conditions through the use of two methods: (i) the addition of sodium ascorbate solution at various concentrations (from 0 to 1 mol/L) to obtain a large range of redox conditions (Pareuil et al., 2008); (ii) N_2 bubbling which allowed the O_2 content and consequently the redox conditions to be modified without the addition of any chemical reagent (Patrick et al., 1973). Both methods were compared in order to demonstrate the advantages and drawbacks of each in studying the influence of redox conditions on element release. In each case, the release of elements was monitored, based on the initial mineralogical composition of slag samples. This study focused on the major elements released which indicated the dissolution of primary solid phases. Mn is present in large amounts and is now known to be an environmental pollutant, due to its potentially toxic effects (*e.g.*, Michalke et al., 2007). For example, Boudissa et al. (2006) studied the level of air and soil Mn contamination near a closed ferromanganese plant: they reported a high soil Mn content, which could become a risk for humans.

Solid phase characterization is essential in understanding the slag behaviour in relation to its mineralogical composition. X-Ray Diffraction (XRD) and Scanning Electron Microscopy with an X-ray microanalysis (SEM-EDS) were performed before and after leaching experiments. The observation of the dissolved solid phases during leaching experiments was done to differentiate and to understand the release mechanisms occurring in both cases. Solid and leachate analyses were completed with Visual MINTEQ calculations allowing the theoretical precipitation of new solid phases to be assessed, without considering the kinetic aspect.

2. Materials and methods

All chemicals were of analytical grade. Solutions were prepared in high-purity de-ionized water (HPW) (Milli-Q system: resistivity 18.2 MΩ cm, TOC $\leq$10 μg/L). All glassware and containers were chemically decontaminated in 10% (v/v) nitric acid beforehand.

2.1. Origin and characterization of slag samples

Two samples of slag produced during a pyrometallurgical process that recycles alkaline batteries were studied. Both samples (S1 and S2) were selected because of their representation of the total amount of battery slag available (50 and 30% respectively).

The slags were produced in block form and were manually crushed to obtain a particle size <1 mm, in order to carry out leaching tests.

After crushing, the total chemical composition of each sample was performed by ACME Analytical Laboratories ltd (Vancouver, Canada). Major elements were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy after a lithium metaborate/tetraborate fusion and nitric acid digestion. Trace elements were determined by Inductively Coupled Plasma Mass Spectrometry after an *aqua regia* digestion (Table 1).

The main mineralogical phases were determined by XRD (Siemens D5000 diffractometer: Cu Kα, 40 kV, 40 mA) on powder samples performed in triplicate at room temperature (20 ± 2 °C). Samples were step-scanned at 0.4 2θ/min. The identification of solid phases was performed using XPert HighScore software (PANalytical). Morphology and chemical analyses of mineralogical phases were done by Scanning Electron Microscopy (Philips XL 30) coupled with an EDS system (accelerating voltage = 20 kV; SERMIEL, Université de Limoges, France); more than fifty SEM-EDS analyses were performed for each sample studied. Electronic microprobe analyses (CAMPARIS, Université de Paris, France) were also performed with two different programs (major elements: 15 kV, 10 nA, spotsize: 1 μm^2, counting time: 10 s; minor/trace elements (Fialin et al., 1999): 30 kV, 500 nA, spotsize: 5 μm^2, counting time: 50 s).

2.2. Leaching experiments in sodium ascorbate solutions

The methodology was adapted from the one previously described for soil samples (Pareuil et al., 2008). Different reductive conditions were obtained with various concentrations of sodium ascorbate (from 0.02 to 1 mol/L), with a liquid/solid ratio L/S = 20 L/kg in 150 mL-HDPE bottles. The slag samples were maintained in suspension by continuous stirring on an orbital shaking table at 250 rpm (IKA-Labortechnik K550 Digital) in the dark (to avoid photo-oxidation phenomena) and at room temperature (22 ± 2 °C). The pH of the suspension was not imposed but monitored throughout the experiments.

A kinetic study was performed beforehand for each slag sample in order to determine the contact time needed to reach stabilized pH, Eh and amounts of elements in the suspensions. Three conditions (HPW, 0.02 mol/L and 1 mol/L sodium ascorbate solutions) were tested in triplicate. Aliquots of the suspensions were taken at

Table 1
Total chemical content of both samples S1 and S2 (ICP/AES and ICP/MS analyses).

Sample	Total Content							
	MnO	SiO_2	MgO	CaO	Al_2O_3	K_2O	Na_2O	Fe_2O_3
wt%								
S1	47.0 ± 3.0	29.1 ± 7.3	5.5 ± 0.3	2.8 ± 0.4	3.4 ± 0.8	2.7 ± 0.4	0.4 ± 0.1	1.0 ± 0.6
S2	70.7 ± 6.1	20.1 ± 3.0	6.8 ± 1.7	1.5 ± 0.4	7.6 ± 0.6	3.7 ± 0.5	0.3 ± 0.1	4.3 ± 2.4
	Cu	Ni	Zn	Cr	Cd	Pb	As	Hg
mg/kg								
S1	212 ± 34	69 ± 50	518 ± 217	41 ± 13	<0.1	0.7 ± 0.1	0.9 ± 0.2	<0.01
S2	1545 ± 735	296 ± 199	437 ± 27	82 ± 8	<0.1	0.4 ± 0.1	1.3 ± 0.1	<0.01