

## SECONDARY PHASES FROM THE ALTERATION OF A PILE OF ZINC-SMELTING SLAG AS INDICATORS OF ENVIRONMENTAL CONDITIONS: AN EXAMPLE FROM ŚWIĘTOCHŁOWICE, UPPER SILESIA, POLAND

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### ABSTRACT

Slags produced by the pyrometallurgical treatment of Zn ore, deposited at the dump in Świętochłowice, in Upper Silesia, southern Poland, are dominated by synthetic analogues of olivine, melilite, pyroxene, feldspars, willemite, zincite and spinel, occurring in various assemblages. Secondary phases either formed at high-temperature or due to weathering are both common at the pile. They include efflorescences of gypsum, epsomite, hexahydrate and bianchite, encrustations of gypsum, anglesite and cerussite, and accumulations of jarosite, goethite and hematite. Two groups are identified: the first one, where sulfates are dominant, is ubiquitous; the second one, of local importance, has originated under conditions varying significantly from one place to another. The weathered phases originate during episodic outflow of water from the pile after rainfall. These mineralogical data and leaching experiments show that, among the primary phases, zincite is most readily weathered, followed by willemite, melilite and the spinel-group phases.

*Keywords:* slag, Zn pyrometallurgy, secondary phases, weathering, sulfates, leaching, Świętochłowice, Poland.

### SOMMAIRE

Les scories issues de la pyrométallurgie du zinc déposées sur les haldes de Świętochłowice, en Haute Silésie, Pologne, comportent diverses paragenèses de minéraux primaires dominées par des analogues synthétiques de l'olivine, la méliélite, la willémite, la zincite, de pyroxènes, de feldspaths et de spinelles. Les phases secondaires, qui comprennent à la fois des phases de haute température et des phases issues de l'altération supergène, sont abondantes sur tout le site. On y reconnaît des efflorescences de gypse, d'epsomite, d'hexahydrate et de bianchite, des encroûtements de gypse, d'anglésite et de cérussite, et des accumulations de jarosite, de goéthite et d'hématite. Ces phases s'organisent en deux groupes, l'un ubiquiste où dominent les sulfates, et l'autre plus local, témoignant des conditions particulières qui peuvent varier selon leurs positions sur le site. Les phases issues de l'altération supergène se forment lors des écoulements qui suivent les épisodes pluvieux. Ces données minéralogiques et les expériences de lixiviation effectuées montrent que parmi les phases primaires, la zincite est le minéral le plus altérable, suivi par la willemite, la méliélite et les spinelles.

*Mots-clés:* pyrométallurgie, zinc, scories, phases secondaires, altération supergène, sulfates, lixiviation, Świętochłowice, Pologne.

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## INTRODUCTION

The waste produced by base-metal smelters mainly consists of slags, dominated by silicate phases. Piles of these wastes are characterized in many cases by metal contents up to several weight % (Parsons *et al.* 2001, Piatak *et al.* 2004). Waste piles originating in 19<sup>th</sup> and 20<sup>th</sup> century are particularly numerous in industrial areas of Eastern Europe (Helios-Rybicka 1996).

The surfaces of waste piles, if not protected by artificial covers such as carried soil or geotextiles, are exposed to natural weathering. The development of finely crystalline sulfates is common on surfaces of mine waste. The mineralogical study of Lottermoser (2005) shows that hydrous sulfates of Ca and Mg (gypsum, epsomite, hexahydrate and blödite) as well as of Fe<sup>3+</sup> (copiapite, römerite) precipitated widely at the Rio Tinto historical smelter site in Spain. In Upper Silesia, Poland, the work of Zainoun (2005) shows the abundance of gypsum as well as a number of other hydrous sulfates growing on the Świętochłowice tailings. As the development of these secondary minerals is an important transitional stage in the mobilization of the material deposited in the pile, detailed knowledge of their occurrences and their relationships with the chemical and mineralogical composition of the piles under a given climate is necessary. However, according to our knowledge, few detailed studies concerning the mineral composition of secondary phases occurring in the smelting waste piles have been published (Ettler *et al.* 2003a, b, Ashley *et al.* 2003, Thiry *et al.* 2002). We present here mineralogical data on the secondary phases developed on the pile of wastes from the zinc smelter of Świętochłowice. In order to identify the mobility of potentially toxic elements (Zn and Pb) from the main Zn-bearing assemblages, analyses of dissolved fractions resulting from laboratory leaching tests lead to a discussion of the sequence of alteration and the formation of the secondary phases. This study complements the description of primary phases in the slags (Puziewicz *et al.* 2007).

## THE STUDY AREA

Świętochłowice is located near the town of Katowice in Upper Silesia (Fig. 1a), in the center of a heavily industrialized area. This region includes numerous coal and metal mines, and also ore-processing industries emitting volatile and particulate constituents that have provoked acidic rainwater. The acidity of rainwater changed from a pH close to 6 between 1970 and 1990 to values between 4 and 5 after 1991 (Hlawiczka *et al.* 2003). The pile at the site covers 15 hectares and reaches 25 m in height. Its trapezoidal form defines two different environments: steep slopes favoring runoff of rainwater, and flat areas (top and base) favoring infiltration. The region is subject to a transitional continental climate, characterized by cold winters with intense episodes of

frost, relatively warm summers, total rainfall of 700 mm/year, and long and regular precipitation of rain or snow from November to May. The mean annual temperature is around 7.5°C.

The pile consists of brown to black fragments of slag from tens of centimeters to meters across, and of scoriaceous material; locally accumulations of ceramic crucible fragments and bricks also are present. The waste is inhomogeneous because of the long interval (1858–1974) of accumulation, during which different ores were used, the zinc-production technology evolved, and because different kinds of wastes were produced at various stages of zinc extraction (Fig. 1b). All those factors (for more details see Puziewicz *et al.* 2007) lead to the heterogeneous bulk composition of the slags (Table 1).

On the contrary, in the central part of the heap, slags were dumped at temperatures high enough to be still liquid. As a consequence, in this part, overall porosity of the waste is low (Fig. 1c) and mainly represented by the discontinuities between the boulders and by millimetric to centimetric vugs and vesicles, or by microcracks 10–100 µm wide at their periphery.

The slags consist of holocrystalline material from 10 µm to several mm in size. The main phases of the slags (Tables 1, 2) are silicates, most commonly synthetic analogues of olivine, melilite, pyroxene, feldspars, willemite and oxides, *e.g.*, of zincite and spinels. The

TABLE 1. BULK CHEMICAL COMPOSITION\* OF SLAGS FROM THE ŚWIĘTOCHŁOWICE DUMP

Sample no. Assemblage <sup>†</sup>	CH06 1	CH21 1	CH18 2	CH20 2	CH10 3	CH24 3
SiO <sub>2</sub> wt.%	23.59	12.43	27.72	33.23	36.46	39.67
TiO <sub>2</sub>	0.13	0.24	0.27	0.20	0.50	0.89
Al <sub>2</sub> O <sub>3</sub>	3.38	14.40	6.62	4.19	15.70	20.69
Fe <sub>2</sub> O <sub>3</sub>	9.86	14.83	29.68	14.45	21.54	18.17
MnO	0.35	0.34	1.21	0.66	0.36	0.34
MgO	3.60	7.74	8.39	10.68	6.19	5.03
CaO	5.89	4.97	20.52	23.27	11.56	9.22
ZnO	47.26	27.96	2.10	1.96	3.38	0.32
PbO	2.04	6.71	0.09	2.29	1.19	0.15
Na <sub>2</sub> O	0.06	0.00	0.00	0.05	0.15	0.27
K <sub>2</sub> O	0.63	0.18	0.28	0.38	1.15	1.34
P <sub>2</sub> O <sub>5</sub>	0.24	0.21	0.21	0.15	0.22	0.35
LOI	6.58	16.34	2.10	7.89	0.37	1.64
Total	103.61	101.38	99.19	99.40	98.77	98.08
S	0.9	2.23	1.27	1.67	0.41	0.42
As ppm	1071	6646	1607	10710	1008	1157
Ba	691	522	1473	1318	2555	1907
Primary phases	mellilite, willemite, kirschsteinite, olivine, zincite, hercynite, franklinite, ilmenite, pyrrhotite		olivine, pyroxene, plagioclase, leucite, zincite, magnetite, sphalerite		kirschsteinite, mellilite, pyroxene, plagioclase, leucite, hercynite, magnetite	
Secondary minerals	gypsum, hexahydrate, epsomite, bianchite, bassanite, willemite, zincite, mimetite, anglesite, cerussite, quartz		gypsum, hexahydrate, epsomite, hematite, barite, plumbian barite, ojuelaite hedyphane		gypsum, hexahydrate, epsomite, hematite	

\* in wt. % unless stated otherwise. <sup>†</sup> Puziewicz *et al.* (2007).

silicate and oxide phases contain variable amounts of Zn, some melilite and K-feldspar also containing Pb. These phases form at least six different assemblages; one of them, including significant zincite and willemite, is probably representative of the melted material before zinc extraction (28–47 wt% ZnO), another only contains 0.3–3.4 wt% ZnO (for more details see Puziewicz *et al.* 2007). Sulfates occur locally and usually in small amounts in the slags.

White to grey efflorescences and incrustations of secondary phases are commonly observed on the pile (Fig. 1d). They form compact coatings millimeters thick on slags and scoriae on variously oriented surfaces. Locally, the white dusty accumulations of secondary phases occur in vugs and cavities located at the slopes of the dump.

#### SAMPLING AND ANALYTICAL METHODS, TERMINOLOGY

The samples were collected between 2000 and 2003 and were taken at every season. Solid phases were characterized by a combination of optical microscopy, scanning electron microscopy (Philips XL–30 equipped with an energy-dispersion (EDS) system at the Université de Limoges) and electron-microprobe analysis (CAMECA SX 50 at the Université de Clermont-Ferrand and SX–100 at the University of Warsaw) using standard conditions (acceleration voltage 15 keV, sample current 18 nA and appropriate standards). For X-ray powder-diffraction studies (XRD), the bulk material was crushed to 20  $\mu\text{m}$  and analyzed with a Siemens D5000 apparatus equipped with a  $\text{CoK}\alpha_1$  anticathode. Bulk-chemical analyses were performed by combination of ICP–MS (inductively coupled plasma – mass spectrometry) for major elements and ICP–AES (inductively coupled plasma – atomic emission spectrometry) for trace elements at the CRPG–CNRS laboratory in Nancy, France. Total digestion of the material was done by melting the sample with  $\text{LiBO}_2$  followed by digestion in nitric acid. Loss of ignition (LOI) was determined by heating the sample for 3 h up to 980°C.

Laboratory leaching experiments were based on the findings of Fällman (1997) and Ettler *et al.* (2003b). Two representative samples that are important carriers of Zn were chosen. Batch experiments were conducted in separate 100 mL HDPE bottles previously washed in acid, containing samples at a solid:liquid ratio of 5g/50 mL. They were disposed on a table shaker (30 rpm, continuous) at ambient temperature (*ca.* 22°C) during 3 hours to 160 days. Two media were tested: (A) acidified water at pH 4.0, daily adjusted with concentrated  $\text{HNO}_3$  and intended to mimic acid rains running on the site (Hlawiczka *et al.* 2003); although this acidity mainly comes from sulfur oxides (thus,  $\text{H}_2\text{SO}_4$ ), we used  $\text{HNO}_3$  because high sulfate amounts have a strong influence on analyses of metallic constituents by atomic absorption (AAS) (Pénilla *et al.* 2005). (B) High-purity water

(MilliQ®) equilibrated with atmospheric air (initial pH 5.6, and let free to vary): these conditions correspond to many standard tests and represent the natural buffering power of alkaline on-site material (Ettler *et al.* 2003b). At 1, 3, 6, 12, 24, 48 hours and 4, 8, 16, 32, 64, 128, 160 days, the content of a given (sacrificial) bottle was filtered through a 0.45  $\mu\text{m}$  membrane filter, then analyzed for Pb and Zn (flame AAS, Varian SpectrAA 220), and for alkaline and alkaline-earth cations and sulfate (ion chromatography, Dionex DX120). At the end of leaching experiments, solid residues were rinsed with high-purity water, dried and analyzed by SEM/BSE and XRD in order to check their surface appearance and mineralogy.

We use the mineralogical terminology in the following for the sake of clarity. The reader should be aware, however, that man-produced phases are *not*

TABLE 2. SECONDARY MINERALS OCCURRING IN THE ŚWIĘTOCHŁOWICE DUMP AND THEIR ABUNDANCE

Name	Theoretical formula	Method of characterization	Presence on the site	Abundance
<b>Sulfates</b>				
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	XRD, EMPA, SEM	ubiquitous	xxxx
hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	XRD, SEM	ubiquitous	xx
epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	XRD, SEM	ubiquitous	xxx
bianchite	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	XRD, SEM	local	xx
barite	$\text{BaSO}_4$	XRD, EMPA, SEM	local	xx
jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	XRD, EMPA	local	xx
anhydrite	$\text{CaSO}_4$	EMPA	ubiquitous	x
bassanite	$2\text{CaSO}_4 \cdot \text{H}_2\text{O}$	EMPA	ubiquitous	x
anglesite	$\text{PbSO}_4$	XRD, EMPA, SEM	local	x
hokutolite	$(\text{Ba}, \text{Pb})\text{SO}_4$	??	local	x
Cu–Zn sulfates	$(\text{Cu}, \text{Zn})\text{SO}_4 \cdot n\text{H}_2\text{O}$	EMPA	local	x
Pb–Fe sulfates	$(\text{Pb}, \text{Fe})\text{SO}_4 \cdot n\text{H}_2\text{O}$	EMPA	local	x
<b>Arsenates</b>				
mimetite	$\text{Pb}_3(\text{AsO}_4)_2\text{Cl}$	EMPA, SEM	local	x
legrandite	$\text{Zn}_3(\text{AsO}_4)_2(\text{OH})(\text{H}_2\text{O})$	EMPA	local	x
hedyphane	$\text{Pb}_2\text{Ca}_2(\text{AsO}_4)_3\text{Cl}$	EMPA, SEM	local	x
ojuelaite	$\text{ZnFe}^{2+}_2(\text{AsO}_4)_2(\text{OH}) \cdot 4\text{H}_2\text{O}$	EMPA	local	x
Fe–Zn arsenate	$(\text{Zn}, \text{Fe})_2(\text{AsO}_4)_2(\text{OH})_2$	EMPA	local	x
<b>Carbonates</b>				
brianyoungite	$\text{Zn}_3(\text{CO}_3)_2\text{SO}_4(\text{OH})_2$	XRD	local	x
cerussite	$\text{PbCO}_3$	XRD, EMPA	local	x
<b>Oxides and hydroxides</b>				
hematite	$\text{Fe}_2\text{O}_3$	XRD, EMPA, SEM	ubiquitous	xxx
goethite	$\text{FeO}(\text{OH})$	XRD, EMPA	local	xx
zincite	$\text{ZnO}$	XRD, EMPA, SEM	local	xx
brucite	$\text{Mg}(\text{OH})_2$	EMPA	local	x
cuprite	$\text{Cu}_2\text{O}$	XRD	local	x
<b>Silicates</b>				
willemite	$\text{ZnSiO}_3$	XRD, EMPA, SEM	local	xx
quartz	$\text{SiO}_2$	XRD, EMPA, SEM	local	xx

XRD: X-ray diffraction, EMPA: electron-microprobe analysis, SEM: scanning electron microscopy.

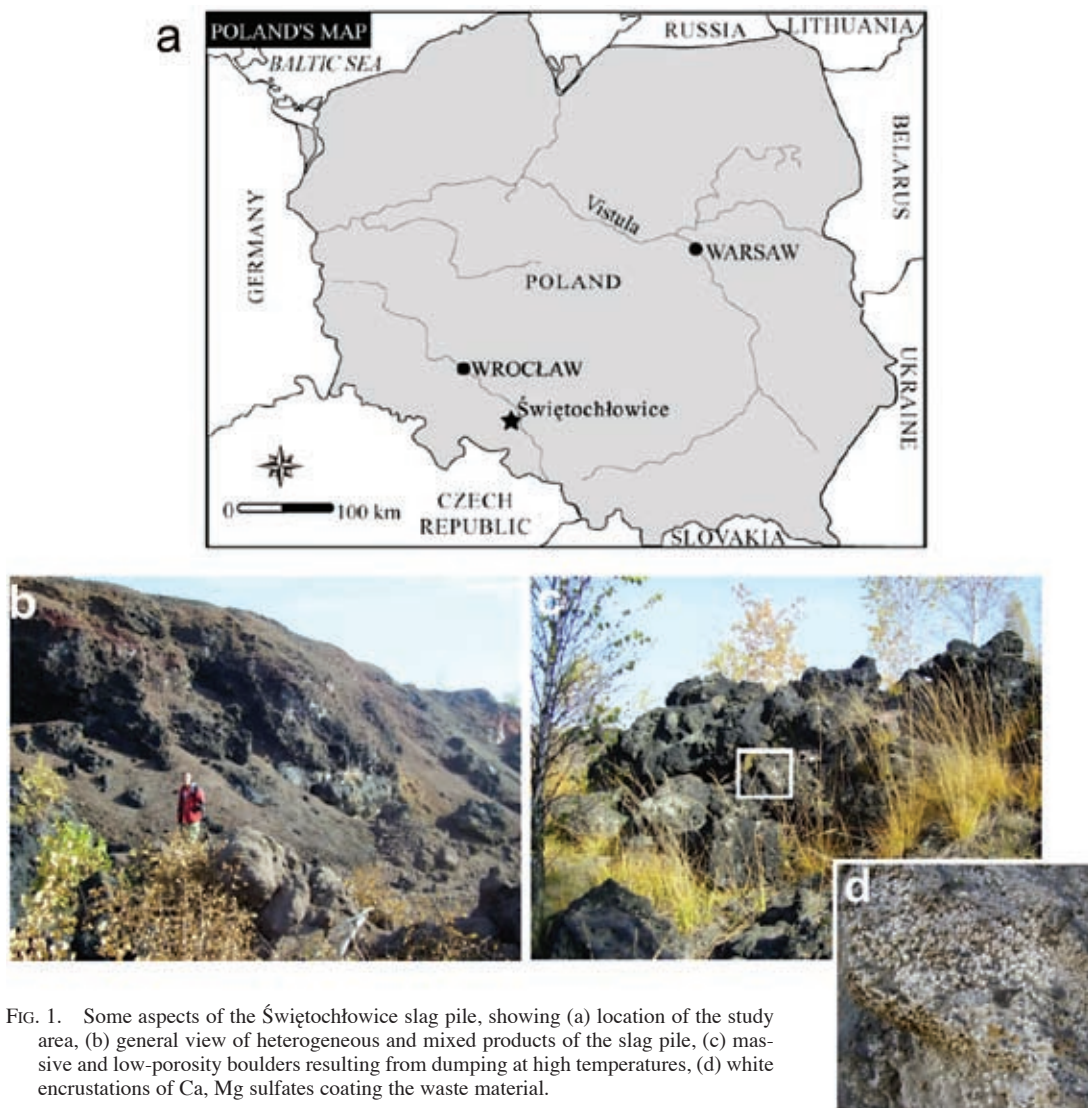


FIG. 1. Some aspects of the Świętochłowice slag pile, showing (a) location of the study area, (b) general view of heterogeneous and mixed products of the slag pile, (c) massive and low-porosity boulders resulting from dumping at high temperatures, (d) white encrustations of Ca, Mg sulfates coating the waste material.

minerals according to the definition of the International Mineralogical Association (Nickel 1995).

#### THE SECONDARY PHASES

Secondary phases are common in the pile (Tables 1, 2). We define the secondary phases as those that originate after the crystallization of the primary ones formed from the silicate melt initially in the slags. The basis for distinguishing between the “primary” and “secondary” is textural and analogous to that used in mineralogy and petrography. Thus, the secondary phases include the phases that might have crystallized at relatively high temperatures after solidification and cooling of the slag (*e.g.*, a secondary willemite II, which cannot form under

conditions of weathering, but during deuteric alteration) as well as those that originated during weathering. In what follows, we use the better-defined term “weathered phases” for the latter.

The secondary phases occur both on slag blocks or smaller fragments and on scoriaceous bases, but the weathered ones are more developed in sheltered locations, where they indiscriminately cover all types of primary material. The accumulations of weathered phases are more abundant during dry periods and less commonly observed in autumn and winter. Secondary, mostly weathering-induced sulfates as well as arsenates, carbonates, oxides or hydroxides and silicates, occur on the pile (Table 2).

The accumulations of secondary phases can be classified according to their appearance on the pile as follows.

(1) White efflorescences, including two varieties: (a) epsomite, gypsum and hexahydrate and (b) bianchite-dominant and subordinate hexahydrate and gypsum. This kind of efflorescence is common, especially in locations protected from rainfall. The assemblage with bianchite is characteristic of Zn-rich slags.

(2) Reddish masses consisting of hematite + gypsum + inherited quartz, which occur in spring after the melting of snow.

(3) Earthy yellowish masses of dominant jarosite + subordinate goethite + small amounts of hematite, occurring in the southern slopes of the pile. The electron-microprobe results reveal the presence of bassanite and inherited quartz in this assemblage. Jarosite is in every case a product of weathering, as no hydrometallurgical treatment (Dutrizac & Jambor 2000) was used in the Świątochłowice smelter.

(4) White compact encrustations consisting of gypsum + anglesite + cerussite + inherited quartz. This is a common encrustation, occurring also on surfaces exposed to rainfall. Locally, it contains scarce, small crystals of arsenates.

(5) Greenish efflorescences of brochantite + cuprite + inherited quartz, observed on separate blocks of slag in the southern part of the pile. They occur in cavities of slags as millimetric crystals; electron-microprobe analyses indicated the presence of Zn sulfates in those assemblages.

Two assemblages of secondary phases occur at the microscopic scale only. These are: (6) cerussite + anglesite + sulfates of Zn, and (7) barite + mimetite.

The most abundant phase is gypsum. Encrustations up to one centimeter thick occur on the slopes and on the surfaces of separated blocks of slags (Fig. 1d). They are observed during both dry and wet periods, but to a lesser extent on surfaces exposed to rainfall during the wet season. Gypsum occurs with various shapes: platy accumulations (*ca.* 1 mm thick) of a few centimeters among blocks of scoria, as millimeter-size plates or cauliflower aggregates on slag surfaces (Figs. 2a, b, c, d). Its chemical composition is close to ideal.

The calcium sulfate corresponding to bassanite occurs in earthy yellowish masses (Table 3, anal. 1). Anhydrite (Table 3, anal. 2) was found in one of the samples studied.

Epsomite (Figs. 2e, f) is present in almost all of the white efflorescences; bianchite was detected by X-ray powder diffraction. A mixture containing 74–85 wt% ZnO and some SO<sub>3</sub> (mixture of hydrozincite and sulfates?) occurs on the surfaces of zincite (Fig. 3a). Sulfates of Cu + Zn (X-ray powder pattern similar to that of brochantite) occur in the greenish efflorescences, and small crystals of Fe + Pb sulfates were found in the vesicles in one of the samples. Jarosite occurs as anhedral grains coating quartz or in aggregates with hematite. It contains up to 6.5 wt% of Al<sub>2</sub>O<sub>3</sub>, 3.8 wt% of PbO and 1.9 wt% of ZnO (Table 3, anal. 3, 4).

Barite occurs in two forms, (1) with Pb arsenates (Fig. 3b) which contain up to 4.3 wt% of PbO and 1.2 wt% of CaO, and (2) in small vesicles in the primary

TABLE 3. CHEMICAL COMPOSITION OF SECONDARY PHASES DEVELOPED AT THE EXPENSE OF SLAG AT ŚWĄTOCHŁOWICE

Anal. no. Phase	1	2	3	4	5	6	7	8	9	10	11
	Anh	Bss	Jrs	Jrs	Brt	Brt	Agl	Agl	Mim	Ojl	Css
SiO <sub>2</sub> wt. %	0.00	0.01	0.56	2.70	0.00	0.00	0.00	0.05	0.01	0.19	0.02
TiO <sub>2</sub>	0.02	0.02	0.16	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.02
Al <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.74	6.48	0.00	0.00	0.00	0.04	0.04	0.53	0.00
FeO	0.01	0.38	41.93*	33.38*	0.00	0.00	0.12	0.50	0.75	27.53*	0.10
MnO	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.05	0.03	2.92	0.03
MgO	0.00	0.03	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	41.24	40.68	0.07	0.10	0.48	1.98	0.14	0.08	0.09	0.03	0.10
BaO	0.00	0.00	0.25	0.25	39.60	61.59	0.00	0.13	0.03	0.00	0.02
CdO	0.00	0.07	0.02	0.02	0.05	0.06	0.00	0.00	1.23	0.00	0.00
PbO	0.00	0.00	1.46	3.84	25.15	0.00	71.63	71.07	74.00	0.04	83.77
ZnO	0.04	0.00	0.44	1.89	4.64	2.34	0.28	1.09	0.25	11.32	0.10
CuO	0.00	0.00	0.08	0.07	0.03	0.00	0.01	0.00	0.01	0.25	0.00
Na <sub>2</sub> O	0.00	0.01	0.55	0.39	0.00	0.00	0.00	0.04	0.19	0.24	0.01
K <sub>2</sub> O	0.04	0.00	6.43	5.93	0.00	0.00	0.46	0.30	1.74	0.01	0.01
P <sub>2</sub> O <sub>5</sub>	n.a.	n.a.	0.15	0.06	0.00	0.00	0.00	0.01	0.43	0.91	0.00
As <sub>2</sub> O <sub>5</sub>	n.a.	n.a.	0.81	0.15	0.22	0.03	0.10	0.00	14.88	48.58	0.00
SO <sub>3</sub>	59.20	54.65	31.73	30.65	30.71	34.34	24.74	23.22	1.49	2.37	0.00
Cl	0.00	0.04	0.00	0.01	0.00	0.00	0.00	0.03	2.91	0.00	0.00
Total	100.56	95.89	85.44	85.95	100.88	100.34	97.48	96.61	98.09	94.92	84.18

n.a.: not sought. \* Fe<sub>2</sub>O<sub>3</sub>. Symbols: Agl: anglesite, Anh: anhydrite, Brt: barite, Bss: bassanite, Css: cerussite, Jrs: jarosite, Mim: mimetite, Ojl: ojuelaite.

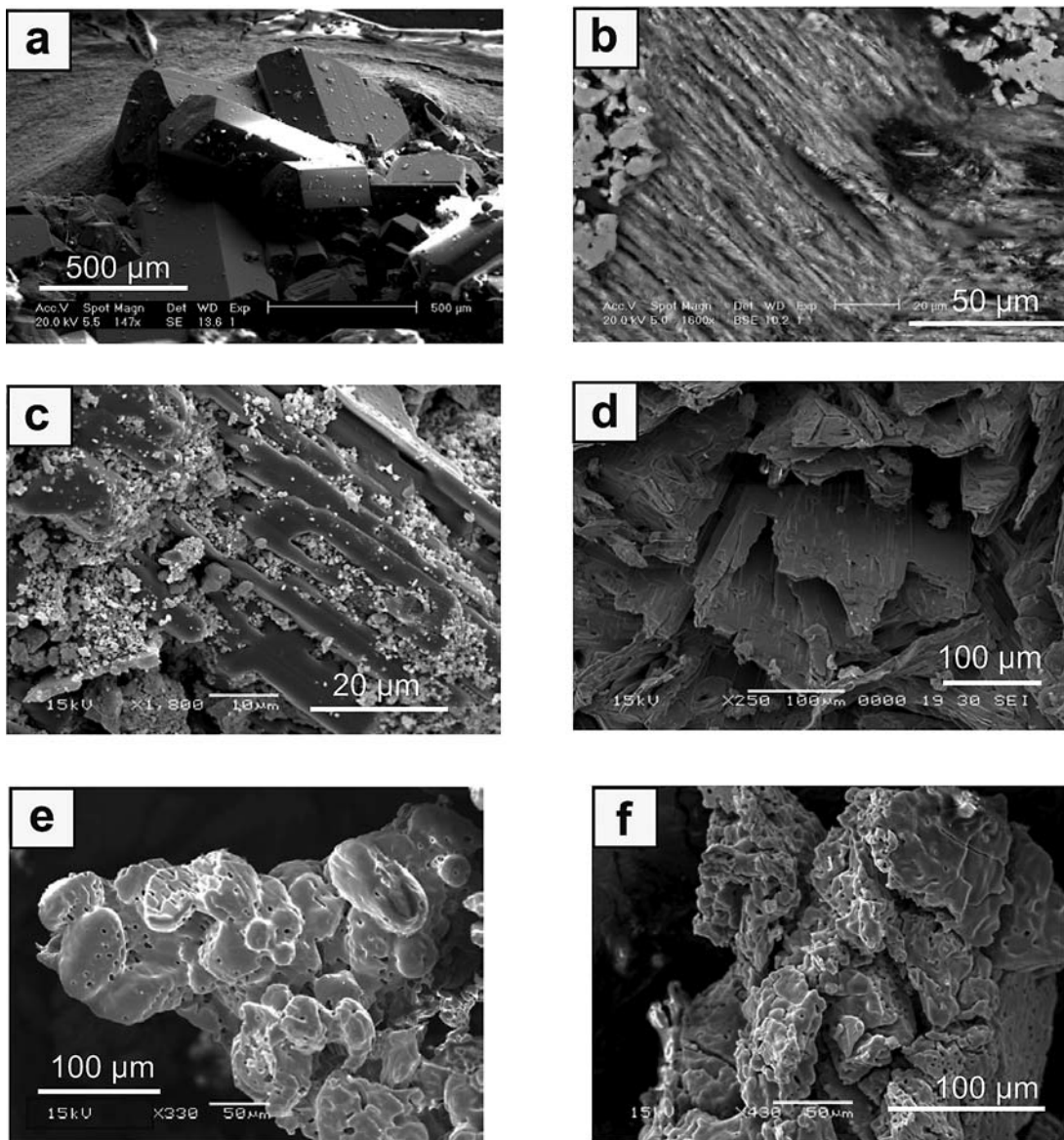
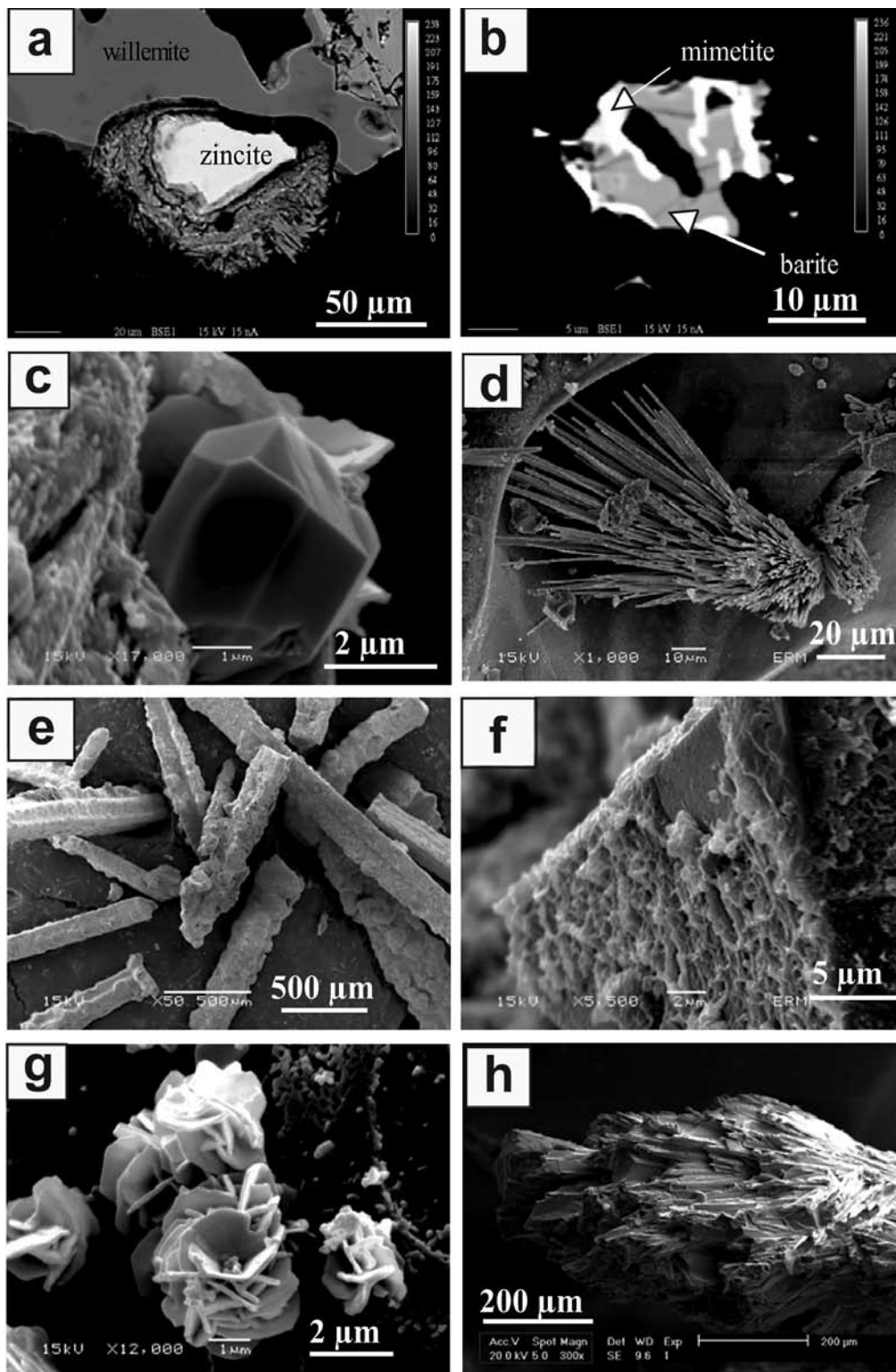


FIG. 2. Habit of gypsum and hexahydrate in the Świętochłowice dump: (a), (b), (c), (d) euhedral crystals, fibrous aggregates, incrustations and platy crystals of gypsum, respectively, (e) and (f) contrasting habits of hexahydrate.

phases among sulfates of Zn, which contain up to 25.2 wt% of PbO, 4.6% ZnO and 2% CaO (Table 3, anal. 5, 6).

Anglesite occurs in white encrustations on the surface of slags together with gypsum; the mineral forms micrometric euhedral crystals (Fig. 3c) or irregular coatings on cerussite. Locally, it contains As

FIG. 3. (a) Zincite covered by products of decomposition (mixture of hydrozincite and sulfates?). (b) Fine intergrowths of barite and mimetite. (c) Crystal of anglesite. (d) Hedyphane needles in a vesicle in slag. (e) Needles of secondary zincite covered by bryanyoungite. (f) Zn-dominant spinel (gahnite) covered by decomposition products containing Si and Al. (g) Small “flowers” of an unknown Zn, Pb, Al, Si phase. (h) Accumulations of secondary willemitite.



(8.7 wt%  $\text{As}_2\text{O}_3$ ) and Zn (up to 4.6% ZnO, Table 3, anal. 7, 8).

Mimetite (Fig. 3b, Table 3, anal. 9) was found in vesicles in the spinel-, melilite- and willemite-bearing slags, and is associated with Zn arsenate. Other arsenates of composition similar to ojealite (Table 3, anal. 10), hedyphane (Fig. 3d) and legrandite occur in the pile, but owing to their small size, their precise characterization was not possible, and electron-microprobe analyses are "contaminated".

A hydrated sulfo-carbonate containing up to 60% ZnO, probably yielding peaks of brianyoungite  $[\text{Zn}_{12}(\text{OH})_{16}(\text{SO}_4)(\text{CO}_3)_3]$  in the X-ray powder pattern, occurs at the margins of zincite crystals or covers the needles of secondary zincite (Fig. 3e). Small (10–20  $\mu\text{m}$ ) grains of cerussite (Table 3, anal. 11) occur, covered by anglesite in some cases.

Hematite occurs as small skeletal crystals or irregular grains, and goethite is a component of earthy yellowish masses occurring in the southern part of the dump. A second generation of zincite occurs as millimetric needles (Fig. 3e) growing on primary Zn-bearing minerals. Euhedral cubic crystals of cuprite were detected in greenish efflorescences.

Secondary silicates are common, but owing to their small size, most of them cannot be conclusively identified. They include: silica polymorphs, a second generation of willemite occurring in yellowish brown crusts consisting of aggregates of acicular crystals, Cu–Zn silicates, Zn-, Fe- and Al-bearing silicates occurring on the surfaces of zincian spinel, and willemite (Figs. 3f, h).

More than 25 secondary phases have been identified, and at least ten others have been suspected in the samples studied. The latter could not be reliably determined because of their size and their variability in composition.

#### BATCH-LEACHING EXPERIMENTS

Artificial extractions are usually performed to assess long-term environmental impacts due to the extent of release of metals, which depends on the nature of solid phases, and on cation mobility in given conditions of weathering (Van der Sloot *et al.* 1996). However, the chemical reagents used never exist under natural conditions, and results of such extractions have to be interpreted with caution. In a given matrix and depending on its composition, such reagents affect solubility, mobility, chemical form and toxicity of the contaminants. Standardized leaching and extraction tests for soils and sediments were discussed by many authors (Sahuquillo *et al.* 2003, and references therein).

In the present study, natural secondary phases were first observed as described above. Then samples of selected primary material were taken. (i) Sample CH21 is representative of phase assemblage 1: meli-

lite, willemite, zincite, zincian spinel with subordinate pyroxene, Pb silicate and ilmenite; (ii) sample CH18 (*cf.* assemblage 2) contains kirschsteinite, spinel, leucite, anandite, pyrrhotite, subordinate pyroxene, olivine, melilite, wollastonite, baddeleyite, and ilmenite, as described in detail by Puziewicz *et al.* (2007).

#### Variations in pH

During test A, it was necessary to add daily some concentrated  $\text{HNO}_3$ . The pH quickly increased to  $6.2 \pm 0.2$  after some hours, whatever the slag sample. In the test B, there was a stabilization (Fig. 4a) at pH  $8.5 \pm 0.3$  (CH21) or  $7.7 \pm 0.2$  (CH18) after *ca.* 64 days. Such an increase in non-buffered solutions of alkaline slags is a common observation (Ettler *et al.* 2003b).

#### Major cations and sulfates

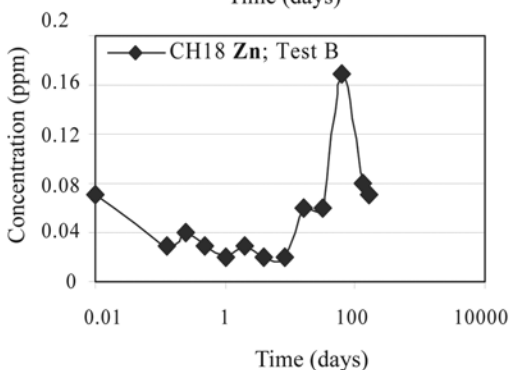
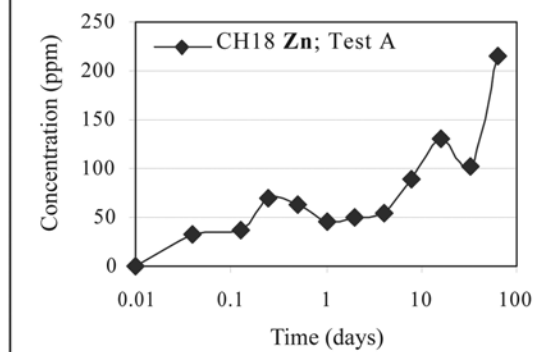
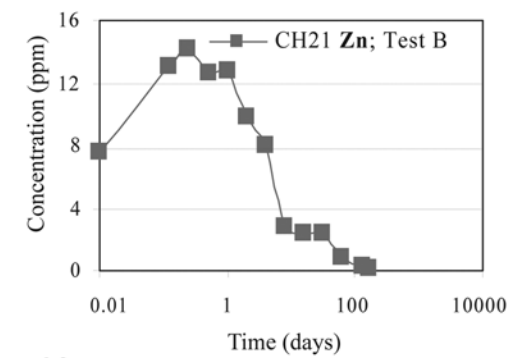
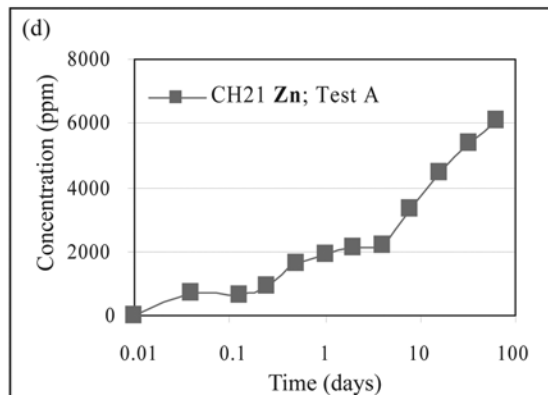
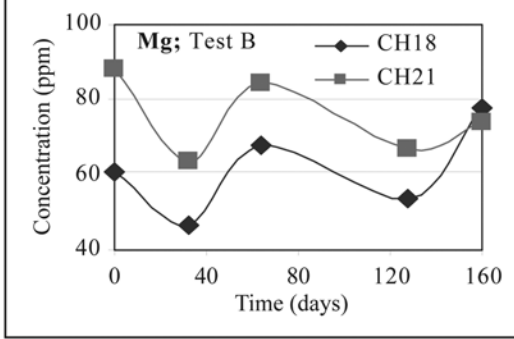
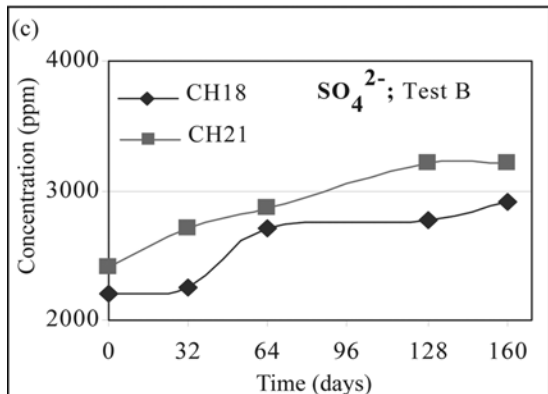
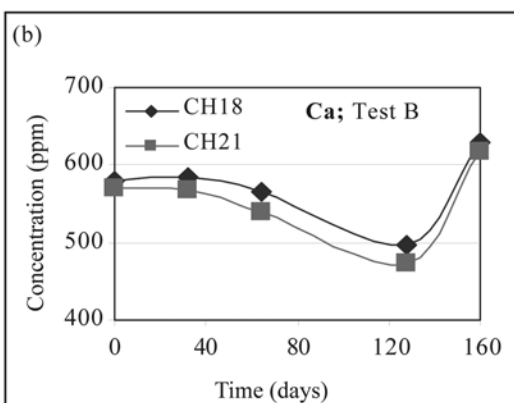
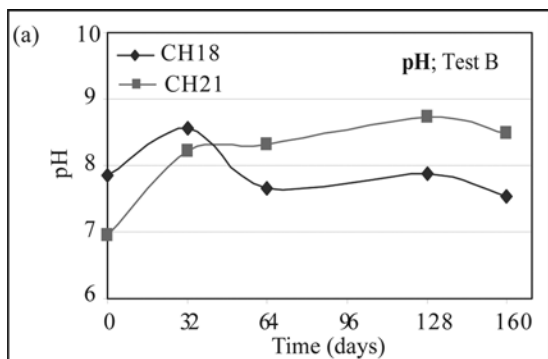
In pure water (test B), the behavior of each cation (Ca, Mg, Na, K) was found to be similar for both samples, with periodical variations related to pH variations as a function of time (Fig. 4b). Sulfate content continuously increased (Fig. 4c), indicating progressive dissolution of a solid phase. During the test A, however, Ca variations showed a regular increase for CH18, but a significant decrease for CH21; for Mg, an almost constant value is observed for CH21, although the initial value dropped for CH18 (Fig. 4b). The high concentration of nitrate in the test A hindered the measurement of sulfate concentration by ion chromatography.

#### Lead and zinc release

The initial Pb and Zn content in each solid phase is very different, and their release is related to both time and solution pH. During test A, their concentration presented similar variations in both samples: a regular increase until day 8, followed by a more rapid step (Fig. 4d for Zn; data not shown for Pb). In pure water (test B), CH18 presented very low values, either for Pb or for Zn concentration in solution ( $\ll 0.1$  ppm; Fig. 4d). For CH21, however, almost constant values were observed,

FIG. 4. Batch-experiment results for samples CH 18 (diamond) and CH21 (square) showing (a) pH variations during test B, (b) evolution of the Ca and Mg concentrations during test B, (c) variations of the  $\text{SO}_4^{2-}$  concentrations during test B, and (d) Zn release from samples CH 21 (29.7% Zn; zincite, willemite and Zn-spinel) and CH 18 (2.1% Zn; monticellite, melilite, leucite and zincian spinel) during test A (left side) and test B (right side). Test A: 64 days in  $\text{HNO}_3$  acidified water at fixed pH 4.0. Test B: 160 days in MilliQ water at an initial pH of 5.6.





with a strong and rapid decrease after 16 days (from 2 to <0.3 ppm for Pb; from 10 to 0.2 ppm for Zn; Fig. 4d).

*Examination of solid phases* before and after leaching provided complementary data needed for interpretations. Under acidic conditions, SEM examinations showed that after the test, grains of spinel are slightly corroded (Fig. 5) and locally coated by a thin layer of gypsum and anglesite. After 64 days at pH 4.0 (test A), gypsum, melilite and zincite disappeared from sample CH21, although anglesite is a neoformed phase. Surface-corrosion figures appeared on the surface of spinel grains, together with anglesite efflorescences (not shown). In sample CH18, gypsum also disappeared, whereas monticellite and spinel grains remained but became highly corroded. In pure water (test B: pH 5.6 and 160 days), corrosion was very limited, and gypsum was not detected on X-ray powder-diffraction patterns. Analyses of the dissolved fraction from test A gave results in agreement with the observation made on natural samples.

The dissolution of gypsum and the subsequent precipitation of anglesite are in good agreement with on-site observations and with the order of thermodynamic solubility (see below). A direct reaction of sulfates with the precipitated zinc (hydr-)oxide can be considered as a probable mechanism, as for atmospheric corrosion of the metal, where the formation of zinc hydroxysulfate  $Zn_4(OH)_6SO_4$  was observed (Graedel 1989). The role of secondary solid phases in controlling zinc speciation in a former metallurgical site was recently emphasized by Nachttegaal *et al.* (2005). They used both 0.1 M  $CaCl_2$  and  $HNO_3$  solutions (at pH 4) to determine the weathering effects under extreme conditions. According to these authors (and previous references cited), the incorporation of Zn within new less soluble solid phases will probably decrease its mobilization during future rainy or flood events. However, the test in pure water gave different results, emphasizing that the presence of bases greatly inhibits the hydrolysis of primary phases.

## DISCUSSION

### *Secondary and weathering phases*

The supergene alteration of the material in the waste pile is made clear by the crystallization of the weathered phases, dominated by sulfates. The acid rainwaters as well as sulfur occurring in the pile contribute presumably to sulfate-producing reactions. Both water-soluble and relatively water-insoluble phases originate during the process. Concentrations of dissolved cations are probably controlled by the insoluble phases, whereas the soluble ones act as a temporary sink for the excess of cations released during the weathering (Jambor *et al.* 2000). The former include compact encrustations of gypsum + anglesite + cerussite, common in the pile and occurring also in places exposed to rainfall. The water-soluble phases are concentrated in dusty efflorescences, which in turn occur typically in places of water outflow protected from rainfall.

According to their phase composition, their abundance and relationships to the primary material, we distinguish: (i) abundant "ubiquitous" phases, present everywhere at the site whatever the chemical and mineralogical characteristics of the surrounding primary phases, and (ii) frequently encountered but less abundant "local" phases, whose occurrence depends on the availability of their structure-forming elements and on the local presence of adequate conditions.

The "ubiquitous" phases are dominated by relatively less soluble phases, and are composed of colloform-like efflorescences of mixtures of  $Mg^{2+}$  or  $Ca^{2+}$  and  $Zn^{2+}$  sulfates, among which gypsum is the most abundant. Their presence everywhere emphasizes significant mobility of the elements concerned, and relatively limited sensitivity to conditions of weathering. Sulfates, especially gypsum, are common in sulfide mining or extraction piles (*e.g.*, Nesbitt & Muir 1998, McGregor *et al.* 1998, Roussel *et al.* 1999). They are considered

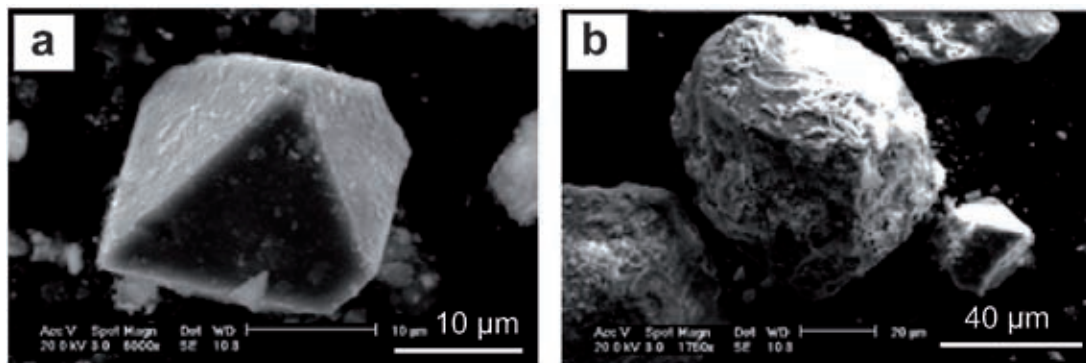


FIG. 5. Grain of gahnite before (a) and after (b) test A.

as “evaporative minerals” by Buckby *et al.* (2003) and by Lottermoser (2005). Gypsum is common in oxidized zones where  $\text{SO}_4^{2-}$  is available (Jambor 1994, Ettler *et al.* 2003a). The presence of jarosite indicates that acidic conditions are maintained, as its transformation into ferrous oxides occurs at  $\text{pH} > 3$  (Dutrizac & Jambor 2000). Even if they are found almost everywhere at the surface of the piles, sulfates are more abundant during summer. Their crystallization is enhanced by oxidizing conditions and a  $\text{pH}$  below 5. The stability of bianchite is restricted to temperatures between 15 and 40°C and a relative humidity of 50–85% (Chou & Seal 2005). Bianchite can transform to goslarite during cold seasons and in more humid locations or periods. In the same way, the association of anhydrite with other sulfates indicates either a highly alkaline context or large variations of temperature and humidity (Eugster *et al.* 1980).

The preservation of these newly formed minerals is favored by weak exposure to effects of seasonal changes in climate or low exposition to rainfall, where they are sheltered by overhangs. During wet periods, as reported in a recent study by España *et al.* (2005), the dissolution of most soluble sulfates such as bianchite lowers the  $\text{pH}$ , affects the release of cations bound to the surroundings, and induces Zn mobilization and a global increase in  $\text{SO}_4$  in streams of waters. The occurrence of variable assemblages of weathering-induced phases in the Świętochłowice dump indicates a wide range of chemical conditions active throughout the site.

The “local” phases are typically the temporary sink of soluble elements. Their nature and the “micro” contexts of their precipitation are different from one location to another, and seem to depend on the specific expositions to weathering agents in the same conditions (grain size, distance of a vug to the surface, microcracks, *etc.*). Usually, these phases appear as small individual crystals coating vugs or fissures (Figs. 3c, g). They only occur a few micrometers (5–50  $\mu\text{m}$ ) from the exposed surface of the material, where water–rock interactions are enhanced by the highly porous texture of their outer part (Fig. 3a). Indeed, Sobanska *et al.* (2000) reported that secondary phases are especially developed where slags are less massive and more porous. These authors evaluated the progress of weathering by enlargement and increase of the roundness of the cavities due to very local hydrolysis. At Świętochłowice, such typical alteration-induced textures were found, underlining the penetration of reaction fronts in the primary phases that appear as corrosion gulfs or replacement figures (Fig. 3a). A portion of the cations is trapped *in situ* by these secondary phases directly growing on the primary ones. These local recombination processes imply a low mobility of the cations concerned. All these observations emphasize that the potential environmental risks of a release of cations at Świętochłowice are limited by the metric size of massive boulders of slag that constitute a great part of the dumps.

#### *Alteration sequences and cation mobility: the chemical perspective*

The phase composition of the primary material has a great influence on patterns of alteration and cation release. Some metal-bearing primary phases appear to be unaffected whatever their particular position, whereas others are deeply weathered. Primary zincite, the most alteration-sensitive mineral, is commonly replaced by a mixture of various sulfates (Fig. 3a) or by a second generation of zincite (Fig. 3e). Dissolution of zincite is more effective at conditions of low  $\text{pH}$  (Bénézech *et al.* 1999). Reprecipitation indicates an increase of  $\text{pH}$  during the earliest stages of weathering. Such deposition of supergene crusts of secondary zincite also was described at the Belovo smelter in Russia by Sidenko *et al.* (2001). At Świętochłowice, primary melilite and kirschsteinite located near the surface of the boulders are partially corroded and coated with fine-grained secondary willemite, in grains 10  $\mu\text{m}$  or less (Fig. 3h).

According to Brugger *et al.* (2003), willemite is stable in hydrothermal environments at temperatures above 100°C under neutral to basic  $\text{pH}$  and oxidized conditions. Its precipitation indicates high activities of  $\text{SiO}_2$ ,  $\text{ZnO}$  and  $\text{O}_2$ , and a low activity of  $\text{CO}_2$ . Thus, the crystallization of a second generation of willemite on the slag surfaces may have been induced by rapid increase in  $\text{pH}$  and the oxidizing action of atmospheric  $\text{O}_2$  during cooling. The acicular form of the willemite suggests rapid crystallization.

When directly exposed to weathering, secondary willemite is less affected, only showing small surface cupules < 5  $\mu\text{m}$  filled by a mixture of undetermined Zn-, Si-, Al-, Fe-bearing secondary phases, whose appearance is similar to those covering the spinel. According to Brugger *et al.* (2003), the immediate environment probably was not acidic. Zincian-spinel-group phases (gahnite, franklinite and Zn-bearing hercynite) are covered by a thin coating (Fig. 2f) containing Si, but it is too thin to yield a reasonable composition. In the conditions prevailing over the pile, we never observed natural corrosion-induced figures on the spinel grains, even if some small deposits of secondary silicates can be observed at their surfaces. Although weathering of Zn-bearing spinels were not studied in a natural environment under a temperate climate, spinel grains in such contexts are usually known to be resistant, as emphasized by Pooley (2004) for chromian spinel or by Soubrand-Colin *et al.* (2005), who studied the natural weathering of Ti-bearing magnetite and chromite in basaltic soils under a cold temperate climate.

At Świętochłowice, we propose the following sequence of alteration of primary Zn-bearing phases from the most resistant to the most fragile phase, *i.e.*, the most soluble: spinel, melilite, willemite, zincite.

However, metallic cations are only temporarily trapped in the secondary phases, as is obvious from

the on-site decrease of abundance of sulfates following rainy episodes. Deposition of minerals due to evaporation, which are scattered throughout the pile and locally present in great quantities, emphasizes the importance of the short, hot and dry periods during summer, facilitating their crystallization. The presence of various assemblages of secondary phases indicates a wide range of pH, oxidizing conditions, sulfate activity and other chemical factors operating throughout the pile. In some places, the observed succession in local assemblages is far from usual: the formation of carbonates is followed by sulfates, and again carbonates are growing on the secondary sulfates. The opposite can also occur: secondary sulfates followed by carbonates and again by sulfates. These numerous lines of evidence of alternation of weathering phases indicate variations of (micro-)conditions of deposition.

If acidic conditions are demonstrated throughout the pile (see above), carbonates are formed under neutral to slightly alkaline conditions (Alpers *et al.* 1994, Eary 1999). For Pb, Ponizovskii & Mironenko (2001) emphasized that the pH required for cerussite precipitation in soils is around six.

The ubiquitous formation of sulfates does not significantly modify the risk and the quantities involved for Zn and Pb release. However, their weathering could locally change the micro-environmental conditions: their dissolution by rainwater at the beginning of autumn locally lowers pH values. It also favors dissolution of willemite in the surroundings. On the other hand, this allows crystallization of a sequence of sulfate-bearing minerals whose solubility differs from the primary products. The data of Morel & Hering (1993) indicate the following order of logS (where S is the molar solubility):  $\text{PbSO}_4$  (-5.0) <  $\text{CaSO}_4$  (-2.3) <  $\text{MgSO}_4$  (-1.0) <  $\text{ZnSO}_4$  (0.5). As a consequence, Pb can be considered as trapped once the crystallization of anglesite occurs. However, according to the proportion of Pb participating in the crystallization of anglesite, it may have only very local effects and simply delay the release of Pb. The relative abundance of gypsum and epsomite and the scarcity of other metal-bearing sulfates are due to high concentrations in Ca and Mg in the primary material, and also to the lower solubility of gypsum and epsomite than of anglesite or Pb-Fe sulfates (Jambor *et al.* 2000), which were only found in small cavities well protected from water runoff on the site.

Hydrous sulfates are the common product of weathering of waste left over after processing of sulfide ores (Kierczak *et al.* 2009). This is because the waste contains abundant sulfur coming from the ore. However, acid rainfall, common in industrialized areas, may contribute significantly to the sulfur budget of the waste dumps, enhancing the rate of weathering and mobilizing metal cations occurring in the waste. The assemblages of hydrous sulfates occurring in the waste piles such as that described in this study are similar to those origi-

nating due to acid drainage of unprocessed sulfide ores (*e.g.*, Hammarstrom *et al.* 2005). In contrast to the latter, the sulfates occurring at the dumps containing technological waste originate by weathering of silicate phases forming the slags, the most important product in the pile of waste. This is the case in the pile at Świętochłowice, which contains holocrystalline slags mainly consisting of silicate and spinel phases.

## CONCLUSIONS

The pile at Świętochłowice collects no water, and the weathering as well as formation of secondary phases are episodic processes initiated after rainfall. Two kinds of sulfate phases are produced during these episodes: the “ubiquitous” ones, occurring everywhere in the pile and mostly relatively insoluble in water (gypsum is the most common), and those of “local” importance, occurring at sites of water outflow from the slopes of the slag heap in sheltered locations, containing also sulfates readily soluble in water (epsomite is the most common). The conditions of precipitation of “local” phases vary from place to place.

An important factor controlling the water penetration and migration in the pile is its porosity. The pebble to boulder size of slag fragments accumulated enhances the infiltration and does not enable the storage of water. The compact texture of the individual boulders and pebbles of slag protects them from water infiltration, which is possible only through the fractures and vugs. Thus, the specific surface of slag material exposed to weathering is not high.

The important factor controlling rates of alteration is the chemical composition of the primary phases. Zincite is the phase most sensitive to weathering in the Zn-Pb slags studied, followed by melilite, kirschsteinite and willemite. As expected, spinel-group materials are the most resistant. Climatic conditions (temperature, intensity of rainfall and its distribution over the year) promote the weathering and affect greatly the rates of reaction. The order of weathering resistance as defined in this study is valid for a relatively cold and wet environment, typical of eastern Europe. Higher temperatures in wetter contexts will allow partial hydrolysis of the most resistant phases, such as spinel.

Studies of industrial dumps are focused on release of potentially toxic elements to the environment. They usually make use of chemical leaching tests. However, these tests differ from the natural conditions because the solution-to-solid ratio is invariably high, and the reaction system is not able to model climatic variations such as storms, short-term variations in humidity and temperature. More complete procedures such as water extractors (Humez *et al.* 1997, Davranche *et al.* 2003), allowing one to simulate the alternation of wet and dry periods, are needed to approach natural conditions. Our study shows, however, that even simple leaching

experiments, if coupled with careful mineralogical observations, may yield reasonable data for assessing the mobility of potentially toxic elements in the pile.

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