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Zinc partitioning between glass and silicate phases in historical and modern lead–zinc metallurgical slags from the Příbram district, Czech Republic

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Abstract – Metallurgical slags of different ages resulting from Pb-metallurgy in the Příbram district (Czech Republic) have been studied. The chemical analysis (EPMA) of melilite, clinopyroxene, olivine and glassy matrix showed the following ZnO concentrations (in wt. %): 3.20–11.93 (melilite), 1.56 (clinopyroxene), 1.29–7.82 (olivine), 1.58–6.58 (glass). The Zn partition coefficient $D = C_s / C_l$ between crystallized phases and coexisting glass was calculated. The values obtained are: 1.96–2.16 (melilite), 0.41 (clinopyroxene) and 0.79–1.19 (olivine). The distribution of zinc between the crystalline phases and glass depends on the phase assemblage, which reflects the blast furnace charge and temperature, as well as the cooling conditions of slags. © 2000 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

Zn partitioning / metallurgical slag / Pb-metallurgy / Příbram / Czech Republic

Résumé – Partage du zinc entre verre et phases silicatées dans des scories historiques et actuelles issues de la métallurgie du plomb dans le district de Příbram, République tchèque. Des scories métallurgiques, d'âges et d'origines différents, issues de la métallurgie du plomb et provenant du district de Příbram en République tchèque ont été étudiées. L'analyse chimique (ME) de mélilite, de clinopyroxène, d'olivine et de matrice vitreuse a révélé les teneurs en ZnO suivantes (en % massique) : 3,20–11,93 (mélilite), 1,56 (clinopyroxène), 1,29–7,82 (olivine), 1,58–6,58 (verre). Le coefficient de partage ($D = C_s / C_l$) entre le cristal et le verre coexistant a été calculé pour chaque espèce. Les valeurs obtenues sont : 1,96–2,16 (mélilite), 0,41 (clinopyroxène) et 0,79–1,19 (olivine). La distribution du zinc entre les phases cristallines et le verre dépend de l'assemblage des phases reflétant la charge du fourneau et la température de fusion, ainsi que la vitesse de refroidissement des scories. © 2000 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

partage du zinc / scorie / métallurgie du plomb / Příbram / République tchèque

Version abrégée

1. Introduction

La pollution des sols et des eaux est souvent liée au stockage des déchets. Récemment, un grand nombre d'études décrivent le comportement des déchets dans des conditions superficielles [2, 7, 9, 10, 12, 14]. Les

scories et les laitiers métallurgiques étudiés sont des déchets de fusion des sources de plomb primaires (minerais) et secondaires (batteries automobiles). Dans ces déchets, le zinc est piégé dans le verre résiduel, d'une part, dans la structure des silicates et des spinelles, d'autre part ; par ailleurs, il existe sous forme de gouttelettes de ZnS. Le but de cet article est de caracté-

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riser la localisation minéralogique du zinc et de calculer son coefficient de partage entre silicates et verre dans des scories et laitiers d'âges différents, provenant de la région de Příbram (*figure*) en République tchèque.

2. Matériel et méthodologie

Quatre types d'échantillons ont été étudiés (*figure*): 1) type **A** – scorie du XIII^e siècle, provenant du site archéologique de Bohutín, 7 km au sud-ouest de Příbram; 2) type **B** – laitier du XVIII^e ou XIX^e siècle, résultant du traitement d'un minerai de Pb, prélevé sur les haldes à Lhota près de Příbram, au voisinage de l'usine métallurgique actuelle; 3) type **C** – laitier du XX^e siècle, résultant du traitement ancien des batteries automobiles, prélevé sur les haldes à Lhota près de Příbram; 4) type **D** – laitier moderne (1998), fourni par le directeur de l'usine métallurgique, résultant du traitement actuel des batteries en utilisant la technologie Varta. Les échantillons ont été étudiés en lames minces et sections polies, par microscopie optique et au microscope électronique à balayage. Les analyses ont été réalisées à la microsonde électronique. Certains échantillons ont été étudiés par la diffraction des rayons X.

3. Résultats et discussion

Les silicates observés sont principalement des mélilites, des clinopyroxènes et des phases à structure type olivine. Ils sont accompagnés de spinelles et d'une phase vitreuse renfermant des inclusions métalliques sous forme de « gouttelettes », de taille souvent inférieure à 1 µm. Trois successions majeures ont été observées: 1) olivine → verre (type **A**); 2) spinelle → mélilite → clinopyroxène → verre à inclusions microscopiques de phases silicatées (type **B**); 3) spinelle → mélilite → olivine → verre (types **C** et **D**).

Les *clinopyroxènes* n'apparaissent que dans le laitier de type B. Ils ne montrent aucune zonation chimique en Zn et peuvent être décrits comme les hedenbergites zincifères (1,56 % ZnO, *tableau I*) [6, 11]. Les *mélilites* sont les phases typiques des laitiers métallurgiques [3, 9]. Elles forment des cristaux prismatiques ou de type « spinifex », sans zonation chimique. Pour les mélilites riches en Zn (laitier type B; 11,93 % ZnO, *tableau I*), leur composition chimique, calculée en termes extrêmes — âkermanite (Ca₂MgSi₂O₇), Fe-âkermanite (Ca₂FeSi₂O₇) et hardystonite (Ca₂ZnSi₂O₇) —, est la suivante: Ak₁₄Fe-Ak₃₇Hard₄₉. Les phases à structure type *olivine* forment des cristaux dendritiques en aiguilles ou de type « spinifex ». Le laitier du type A est principalement composé d'une fayalite zincifère à 7,82 % ZnO,

tandis que les autres types de laitiers contiennent les olivines riches en Ca et proches de la Fe-monticellite (*tableau I*). Les *spinelles* sont les phases les plus riches en Zn (souvent plus de 18 % ZnO). Par suite de leur cristallisation précoce, ils sont piégés par d'autres minéraux, surtout par les mélilites. N'ayant aucun contact direct avec le verre interstitiel, les spinelles ne sont pas pris en compte dans l'étude du partage de Zn. Dans le verre interstitiel, les concentrations en Zn peuvent atteindre 7 % ZnO environ (*tableau I*). Le verre interstitiel au contact des silicates a été analysé. Afin d'éliminer la contamination par les gouttelettes métalliques, seules les analyses reproductibles ont été retenues. La présence de Zn dans toutes les espèces étudiées suggère que Zn²⁺ se substitue à Fe²⁺ en site octaédrique, à cause des rayons ioniques similaires de ces deux cations [4, 5].

Les coefficients de partage (*tableau II*) ont été calculés en utilisant la relation [1]: $D = C_s / C_l$, où C_s et C_l sont les concentrations en ZnO (% massique) respectivement dans une phase cristallisée (s) et dans le verre (l). Dans les conditions données, la valeur du coefficient de partage dépendra surtout de la structure et la composition chimique des phases cristallisées et du liquide résiduel [13]. Pour les *mélilites* de tous les types d'échantillons, les coefficients de distribution de Zn sont supérieurs à 1,9. Des valeurs similaires ont été notées par Wearing [15] pour les mélilites des laitiers de la métallurgie de Sn. Les *clinopyroxènes* indiquent une valeur de D inférieure à l'unité ($D = 0,4$). Pour les phases de type *olivine*, les valeurs de D varient autour de l'unité. Dans les scories du Moyen Âge, la fayalite (représentant la seule phase silicatée à l'état cristallin) est enrichie en Zn par rapport au verre environnant ($D = 1,2$). En revanche, les phases à structure type olivine provenant des laitiers C et D présentent des valeurs de D de 0,9 et 0,8 respectivement.

4. Conclusion

Cette étude confirme que, pendant le refroidissement des laitiers métallurgiques, le zinc est piégé dans la structure des phases oxydées et silicatées (spinelle, mélilite, clinopyroxène, phases à structure type olivine), où il se substitue à Fe²⁺ en sites octaédriques. Le coefficient de partage du zinc entre phases cristallisées et verre varie entre 2 environ pour la mélilite et 0,4 pour le clinopyroxène. La distribution du zinc entre les phases cristallines et le verre dépend de l'assemblage des phases, reflétant la charge du fourneau et la température de fusion, ainsi que la vitesse de refroidissement des scories.

1. Introduction

Pollution of soil and water is often related to dumped wastes. In this respect, a large number of environmental

studies are focused on the behaviour of waste under surface conditions. Municipal solid waste incinerator (MSWI) bottom ash, metallurgical slags and mine tail-

ings may represent important pollution sources [2, 7, 9, 10, 12, 14]. This article concerns Pb–Zn metallurgical slags — a type of waste resulting from the fusion of primary and secondary Pb-sources. This material contains important amounts of heavy metals incorporated in crystallized and glassy phases.

During the metallurgical smelting process, the majority of recovered metals (Pb, Ag, Cu) are concentrated in liquid form as nearly pure metal and/or as sulphide ‘matte’ at the bottom of the blast furnace. However, almost all the zinc is vaporized or dissolved in the liquid silicate slag floating on the dense matte and liquid metals [4]. In the silicate slag, zinc is present in three forms: (i) quenched sulphide droplets, (ii) silicates and oxides and (iii) silicate glass. This article is devoted to crystal/melt partitioning of Zn in slag samples of different ages, resulting from metallurgical activity in the region of Příbram (Czech Republic). The basic hypothesis is that, because of quenching, the diffusion rate of zinc in melt is negligible. Consequently, in the same sample, the apparent partition coefficients may be calculated for different stages of the crystallization sequence knowing respectively the Zn concentrations in the crystalline solid phase and coexisting glass.

2. Material and methods

Four different slag types were studied, originating from different sites (*figure*) located in the mining district of Příbram, known for its polymetallic vein deposits (with mainly Ag, Pb, Zn, As, Sb and Sn):

- **A-type slag:** dated from XIIIth century, it has been found in archaeological excavations near Bohutín, about 7 km southwest of Příbram; this slag results from the smelting of Pb–Ag ores in primitive blast furnaces,

probably at a relatively low temperature (use of charcoal for heating) and without a Ca source in the furnace charge; samples occur as fragments of vitrified material of several centimetres in size;

- **B-type slag:** it is one or two centuries old (XVIIIth to XIXth century); it derives from Pb-ore processing and smelting; slag casts (size about 30 cm) have a cone-like shape and sometimes a sulphide ‘matte’ at their base; they were sampled on the dumps at Lhota near Příbram, in the vicinity of the Příbram smelter;

- **C-type slag:** only few decades old (XXth century); it is a by-product of past processing of car batteries and forms ‘eaves-shaped’ elongated blocks about 30 cm in length; it has been sampled on the dumps at Lhota near Příbram;

- **D-type slag:** modern slag results from the present-day battery processing and smelting; a huge sample was provided in December 1998 by the courtesy of the director of Příbram smelter (Kovohut Příbram, a.s.).

Thin and polished sections of slag samples were studied in transmitted and reflected light by optical microscopy; then by a Jeol JSM 6400 scanning electron microscope (SEM, ESEM—université d’Orléans). Solid phase analyses were carried out using a Cameca SX-50 electron-microprobe analyser (EPMA, BRGM–CNRS Orléans) under the following analytical conditions: accelerating voltage 15 kV, beam current 12 nA, counting time 8 s on peak and background except for Pb (16 s); set of standards: albite (Si, Na), K-feldspar (K), forsterite (Mg), hematite (Fe), andradite (Ca), barite (Ba), apatite (P), zincite (Zn), galena (Pb), Cr₂O₃ (Cr), NiO (Ni), pyrite (S), vanadinite (Cl), synthetic MnTiO₃ (Ti, Mn) and Al₂O₃ (Al). In some cases, the phase composition of studied samples was determined using X-ray powder diffractometer (XRD) with Cu K α radiation; the measurements were done in step-scan mode over the

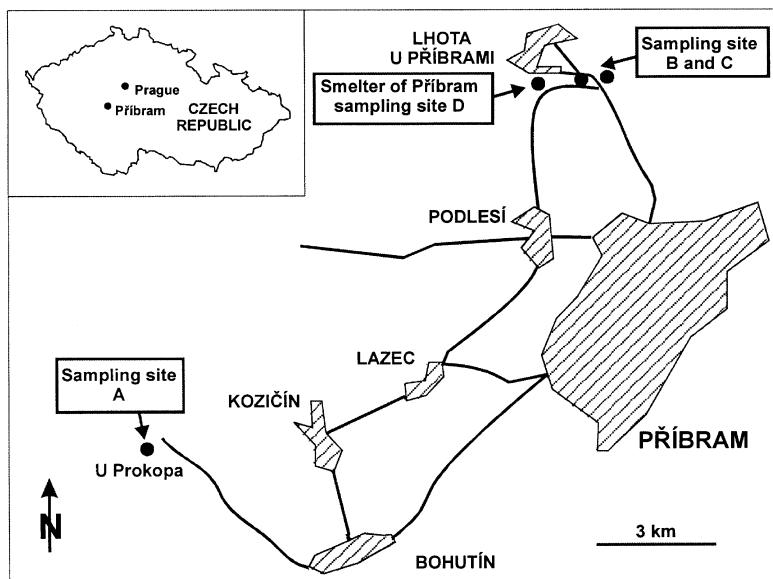


Figure. Geographic location of mining district of Příbram with sampling sites.

Figure. Position géographique du district minier de Příbram et localisation des sites d'échantillonnage.

range 5–80° 2 θ in steps of 0.01° and with a counting time of 10 s.

3. Results and discussion

3.1. Mineralogy

3.1.1. Overview

High-temperature Ca–Fe aluminosilicates crystallizing at about 1300 °C (melilites, clinopyroxenes, olivine-type phases) accompanied by oxides (spinel), rare sulphides and metallic phases are the major crystallized components of the studied slags. Only oxides and silicates are the subject of this paper.

Three major phase assemblages were observed, with the following crystallization sequences: 1) olivine → glass (A-type slag); 2) spinel → melilite → clinopyroxene → interstitial glass with sub-microscopic inclusions of silicates (B-type slag); 3) spinel → melilite → olivine → glass (C-type and D-type slags). The main differences in mineralogical and chemical composition of the different slags are:

- absence of Ca-rich silicates (clinopyroxene, melilite) in the A-type slag (lack of addition of CaCO₃ as a melting agent in the Middle Ages) while, at least, one of these Ca-bearing phases occurs in other types of slag;
- presence of minor Cl concentration in the glass of C-type slag, resulting from the fusion of car batteries with their PVC cases;
- occurrence of Na-bearing phases (melilites in C and D-type) due to the use of sodium compounds in the Harris refining technological process from 1941 to 1997 [8].

3.1.2. Clinopyroxenes

Clinopyroxenes were observed only in B-type slags, in the central parts of casts where cooling was relatively slow. They occur as green phenocrysts with a maximum length of several hundreds of microns. The compositional profile through a clinopyroxene crystal reveals a slight zoning with a border enriched in Fe and Al and depleted in Si and Mg. However, there is no difference in Zn concentration between the crystal core and the rim. The composition of the studied clinopyroxene is rather complex (table I). A hedenbergite end-member (CaFeSi₂O₆) is the prevailing component with 1.56 wt. % ZnO. Essene and Peacor [6] plotted the Zn-bearing clinopyroxenes into the compositional space of three end-members: diopside + hedenbergite (Ca(Mg,Fe)Si₂O₆) — johannsenite (CaMnSi₂O₆) — petedunnite (CaZnSi₂O₆). Referring to these end-members, the crystal-chemical formula of the studied clinopyroxene can be expressed as (Di + Hd)₉₀Jh₅Pe₅.

3.1.3. Melilites

Melilites are common in slags [3, 9]. In the studied samples they occur either as comb-shaped irregular

prisms (harrisitic crystals), or as phenocrysts of hundreds of μm in size, without chemical zonation. Their composition is given in table I. They contain mainly iron-åkermanite (Ca₂FeSi₂O₇) and åkermanite (Ca₂MgSi₂O₇), with an important amount of hardystonite (Ca₂ZnSi₂O₇). The melilite with the highest ZnO content corresponds to a B-type slag and its composition, taking into account the above-mentioned end-members, can be expressed as Ak₁₄Fe-Ak₃₇Hard₄₉.

3.1.4. Olivine-type phases

Olivine-type phases are the last silicates crystallizing from the liquid in the C- and D-type slags. They form small needles or dendrites, often difficult to analyse by EPMA, due to their size. However, in A-type Middle Ages slag, olivine appeared early and its chemical composition corresponds to Zn-bearing fayalite with up to 7.82 wt. % of ZnO (the fayalite structure has been confirmed by XRD). Other Zn-bearing fayalites found by Chaudhuri and Newesely [4] in Harz Mountain metallurgical slags contain up to 12.75 wt. % of ZnO. Zn substitutes for Fe²⁺ in the fayalite crystal structure. In CaO-rich slags, 'olivine-type' phases are similar to Fe-monticellite (confirmed by XRD) (table I). They contain lower Zn concentrations than fayalite present in the A-type slags (table I).

3.1.5. Spinel

Spinel, when present, appear early in the crystallization sequence forming euhedral crystals of several μm in size. They are embedded in later phases such as melilites. Spinel with coexisting glass were not observed and therefore they are not suitable for crystal/liquid partitioning calculation. They concentrate important amounts of zinc (> 18 wt. % of ZnO), are very often zoned, and correspond to a complex solid solution of spinel, hercynite, gahnite, and magnetite, with elevated percentages of Cr-bearing end-members for modern slags.

3.1.6. Metallic phases and sulphides

Metallic phases and sulphides are important concentrators of heavy metals in slags, where they occur as inclusions trapped in glass. The EPMA study revealed the presence of metallic Pb, Cu and Sb, galena, sphalerite/wurtzite, pyrrhotite, bornite, and different complex alloys and inter-metallic compounds of Sb, Sn, Cu, As and Pb.

3.1.7. Glass

Glass, recognizable by its amorphous character, exists in two different locations: (i) at the chilled margin and (ii) as interstitial glass between silicate crystals. With respect to the crystal/melt partition study, only glass in direct contact with clinopyroxene, melilite and olivine has been taken into consideration (table I). In order to eliminate contamination by sub-microscopic inclusions

Table I. Selected microprobe analyses of crystalline phases and glass. The structural formulae of crystalline phases were calculated on the basis of 4 (olivine), 6 (clinopyroxene) and 7 (melilite) oxygens; (**A**: Middle Ages slag, **B**: slag from ore processing, **C**: slag from historical battery processing, **D**: slag from modern battery processing).**Tableau I.** Analyses à la microsonde électronique des phases cristallines et du verre. La formule structurale des phases cristallines a été calculée sur la base de 4 (olivine), 6 (clinopyroxène) et 7 (mélilite) oxygènes; (**A**: scorie du Moyen Âge, **B**: laitier du traitement des minerais, **C**: laitier du traitement historique des batteries, **D**: laitier du traitement actuel des batteries).

slag type	A	A	B	B	B	B	C	C	C	D	D	D
phase	olivine	glass	clinopyroxene	glass	melilite	glass	melilite	glass	olivine	melilite	glass	olivine
SiO ₂	31.13	39.44	42.34	31.54	39.67	30.77	39.84	30.39	31.35	39.54	31.99	30.16
TiO ₂	0.04	0.48	0.79	0.00	0.00	0.03	0.08	1.04	0.10	0.00	0.54	0.25
Al ₂ O ₃	0.36	5.58	8.66	1.88	1.77	0.20	5.38	15.62	0.04	7.44	6.25	0.89
FeO	45.39	14.58	21.72	45.67	8.10	51.32	10.84	30.80	39.20	8.37	29.66	42.52
MnO	8.22	2.45	1.30	3.87	0.71	4.67	0.56	0.66	2.72	0.04	0.92	1.60
MgO	4.50	0.27	1.96	0.42	1.74	0.88	2.31	0.06	2.65	3.53	2.97	4.24
CaO	0.49	5.12	22.50	10.80	34.59	7.86	34.63	14.15	21.95	34.67	20.65	17.52
Na ₂ O	0.11	0.47	0.08	0.24	0.45	0.10	2.06	0.71	0.11	2.57	0.81	0.13
K ₂ O	0.17	1.43	0.09	0.45	0.20	0.03	0.11	0.28	0.03	0.11	0.43	0.04
BaO	0.66	4.56	0.00	0.00	0.00	0.00	0.00	1.05	0.00	0.00	0.81	0.16
P ₂ O ₅	0.06	0.65	0.33	0.23	0.33	0.05	0.38	0.49	0.23	0.45	0.50	0.32
Cr ₂ O ₃	0.12	0.00	0.04	0.00	0.00	0.02	0.00	0.00	0.00	0.06	0.00	0.03
NiO	0.03	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.18
ZnO	7.82	6.58	1.56	3.77	11.93	5.53	3.40	1.58	1.43	3.20	1.63	1.29
PbO	0.35	16.43	0.00	0.32	0.52	0.12	0.20	0.44	0.00	0.03	0.06	0.08
SO ₃	0.03	1.42	0.00	0.00	0.03	0.00	0.02	1.70	0.00	0.00	0.24	0.11
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.79	0.00	0.00	0.48	0.00
Total	99.47	99.45	101.35	99.22	100.04	101.56	99.81	99.75	99.79	100.01	98.06	99.51
Si	1.035		1.708		1.998		1.936		0.993	1.888		0.977
Ti	0.000		0.024		0.000		0.003		0.000	0.000		0.000
Al	0.000		0.412		0.105		0.308		0.000	0.419		0.000
Fe	1.262		0.733		0.341		0.441		1.038	0.334		1.152
Mn	0.232		0.044		0.030		0.023		0.073	0.001		0.044
Mg	0.223		0.118		0.131		0.167		0.125	0.251		0.205
Ca	0.018		0.973		1.866		1.803		0.745	1.774		0.608
Na	0.000		0.006		0.044		0.194		0.000	0.238		0.000
K	0.000		0.000		0.013		0.007		0.000	0.007		0.000
Cr	0.003		0.001		0.000		0.000		0.000	0.000		0.001
Ni	0.001		0.000		0.000		0.000		0.000	0.000		0.005
Zn	0.192		0.046		0.444		0.122		0.033	0.113		0.031
Pb	0.000		0.000		0.007		0.003		0.000	0.000		0.000

of ZnS, only reproducible data for a given glass/crystal pair have been considered.

3.2. Zinc site occupancy

Simplified general formulae of studied phases are the following: XYZ_2O_6 (clinopyroxene), $X_2YZ_2O_7$ (melilite) and $XYZO_4$ (olivine), where X is a large cation, eight co-ordinated, Y an octahedral intermediate-sized cation, and Z a tetrahedral small-sized cation [15]. In all silicates (clinopyroxene, melilite and olivine) Zn^{2+} (ionic radius: 0.74 Å) will very likely prefer the octahedral Y sites and substitute for Fe^{2+} (ionic radius: 0.76 Å) [4]. In all these relevant cases, a limited miscibility between Fe and Zn end-members may be supposed. For example, the solid solution series between Fe_2SiO_4 (fayalite) and Zn_2SiO_4 (willemite) extends from the fayalite end-member up to 17 mol % Zn_2SiO_4 (i.e. 13.37 wt. % of ZnO) [5].

3.3. Partition coefficients

The partition (or distribution) coefficient is defined as $D = C_s / C_l$, where C_s is the concentration of the studied

element in the crystal and C_l is its concentration in the liquid [1]. Partition coefficients for Zn (*table II*) were calculated using the formula $D = (ZnO \text{ (wt. \%)} \text{ in crystal}) / (ZnO \text{ (wt. \%)} \text{ in glass})$. In general, for a given pressure, the partition coefficient depends (*i*) on the structure and chemical composition of both melts and crystals and (*ii*) on temperature (about 1 300 °C for recent slags but lower for slags of the Middle Ages). The 'structural-compositional' dependence is the most important factor [13].

Although the partition coefficient for *spinel*s was impossible to calculate, one may suppose D values sig-

Table II. ZnO crystal/glass partition coefficients.**Tableau II.** Les coefficients de partage de ZnO entre cristaux et verre.

slag type	A	B	C	D
D (cpx-glass)	—	0.41	—	—
D (mel-glass)	—	2.16	2.15	1.96
D (ol-glass)	1.19	—	0.91	0.79

nificantly higher than 1, with relevance to the compatible behaviour of Zn with spinel structure.

Melilites show D values of about 2. Similar values for Zn crystal/liquid partition coefficients were also obtained by Wearing [15] for melilites from tin slags. Both these results reveal that Zn is compatible with melilite structure and hence its concentration in the residual melt will be depleted during melilite crystallization. However, due to a moderately high D value, enough Zn will remain in the liquid to allow a significant trapping of this element in later crystallized phases.

The partition coefficient for *clinopyroxene* shows a lack of compatibility of Zn with its structure ($D = 0.4$). In agreement with the data of Wearing [15], the melt becomes enriched in Zn during the clinopyroxene crystallization. Despite this 'incompatibility', a significant amount of Zn enters into the clinopyroxene structure. According to Morimoto [11], the Zn concentration, given in this study (1.56 wt. % ZnO, *i.e.* 0.05 cations per formula unit), is sufficient to permit use of the name 'zincian hedenbergite' for this phase.

The partition coefficient calculated for *olivine* is close to 1. Slightly compatible behaviour was noticed for Zn in the system fayalite-melt from the XIIIth century slag ($D = 1.2$) while in the case of olivine-type phases from C- and D-type slags, partition coefficients are respectively 0.9 and 0.8. For fayalites in a copper slag, Wearing [15] calculated Zn partition coefficients reaching

2.9. This discrepancy may result from differences in fayalite growth rates, variation of D with melt structure, etc.

4. Conclusions

This study confirms that during the cooling of metallurgical slags, Zn enters into the crystal structures of oxides and silicates (spinel, melilite, clinopyroxene and olivine), due to the substitution for Fe^{2+} in octahedral sites. The distribution of zinc between silicates and glass depends on the phase assemblage (nature and probably texture) which reflects blast furnace charge and temperature, as well as the cooling conditions of the slags. The calculated crystal/glass Zn partition coefficient shows a rather compatible behaviour with respect to melilite, and rather incompatible behaviour with clinopyroxene while olivine-type phases display a D value close to 1.

During the cooling of the melt, zinc enters first into the spinel structure. Melilite starts to nucleate simultaneously with spinel and also concentrates Zn. In contrast, the calculated D values for late crystallized phases (clinopyroxene in the B-type slag or olivine in C- and D-type slags) are lower than 1, indicating Zn enrichment in the residual melt.

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References

- [1] Albarède F., Bottinga Y., Kinetic disequilibrium in trace element partitioning between phenocrysts and host lava, *Geochim. Cosmochim. Acta* 36 (1972) 141–156.
- [2] Baranger P., Azaroual M., Lanini S., Piantone P., Freyssinet P., Modelling the weathering of a bottom-ash heap, in: Méhu J., Grelrier-Volatiér L., Burleigh T. (Eds.), *Waste stabilization and environment*, Lyon, France, 1999, pp. 79–83.
- [3] Butler B.C.M., Al-rich pyroxene and melilite in a blast furnace slag and a comparison with the Allende meteorite, *Mineral. Mag.* 41 (1977) 493–499.
- [4] Chaudhuri J.N.B., Newesely H., Mineralogical characterization of old Harz Mountain slags, *Can. Metall. Quart.* 32 (1993) 1–12.
- [5] Ericsson T., Filippidis A., Cation ordering in the limited solid solution $\text{Fe}_2\text{SiO}_4\text{--Zn}_2\text{SiO}_4$, *Am. Mineral.* 71 (1986) 1502–1509.
- [6] Essene E.J., Peacor D.R., Petedunnite ($\text{CaZnSi}_2\text{O}_7$), a new zinc clinopyroxene from Franklin, New Jersey, and phase equilibria for zincian pyroxenes, *Am. Mineral.* 72 (1987) 157–166.
- [7] Eusden J.D., Eighmy T.T., Hockert K., Holland E., Marsella K., Petrogenesis of municipal solid waste combustion bottom ash, *Appl. Geochem.* 14 (1999) 1073–1091.
- [8] Hamppejs V., Jubilee of the smelter of Příbram, *Oblastní muzeum Podbrdská v Příbrami*, 1971, 268 p. (in Czech).
- [9] Kucha H., Martens A., Ottenburgs R., De Vos W., Viaene W., Primary minerals of Zn–Pb mining and metallurgical dumps and their environmental behaviour at Plombières, Belgium, *Environ. Geol.* 27 (1996) 1–15.
- [10] Mandin D., Van der Sloot H.A., Gervais C., Barna R., Méhu J., Valorization of lead–zinc primary smelters slags, in: Goumans J.J.J.M., Senden G.J., Van der Sloot H.A. (Eds.), *Waste materials in construction*, Houthem, St. Gerlach-Netherlands, 1997, pp. 617–629.
- [11] Morimoto N., Nomenclature of pyroxenes, *Mineral. Mag.* 52 (1988) 535–550.
- [12] Morin G., Ostergren J.D., Juillot F., Ildefonse P., Calas G., Brown G.E., XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption processes, *Am. Mineral.* 84 (1999) 420–434.
- [13] Mysen B.O., Virgo D., Trace element partitioning and melt structure: an experimental study at 1 atm. pressure, *Geochim. Cosmochim. Acta* 44 (1980) 1917–1930.
- [14] Shu J., Bradshaw A.D., The containment of toxic wastes. I. Long term metal movement in soils over a covered metalliferous waste heap at parc lead-zinc mine, North Wales, *Environ. Pollut.* 90 (1995) 371–377.
- [15] Wearing E., Crystal-liquid partition coefficients for pyroxene, spinels, and melilites, in slags, *Mineral. Mag.* 47 (1983) 335–345.