

RELATION BETWEEN THE ZN(II) CHEMICAL SPECIATION AND ITS ACID LEACHING FROM FINE GRAINED METALLURGICAL WASTES

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VZTAH MEZI CHEMICKOU SPECIACÍ ZN(II) A JEHO KYSELÝM LOUŽENÍM Z JEMNÝCH METALURGICKÝCH ODPADŮ

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Abstrakt

Pomocí sekvenčně extrakční metody chemické speciace byly určeny formy zinku ve vysokopecních a ocelářenských kalech. Ve vysokopecních kalech je zinek přítomen převážně ve formě iontovýměnné a povrchově okludované a proto může být jeho separace kyselým loužením úspěšná. Tyto předpoklady byly potvrzeny při studiu heterogenních acidobazických rovnováh při diskontinuálním statickém vyluhování za mírně kyselých podmínek - $c(\text{HCl}) \text{ max. } 0,1 \text{ mol} \cdot \text{dm}^{-3}$, kdy se vyloužilo 77% zinku a železo prakticky nepřecházelo do roztoku.

U ocelářenského kalu nebyla nalezena jednoznačná souvislost mezi chemickou speciací a kyselým loužením. Při vyluhování tohoto materiálu se ustavuje pufrální rovnováha při $\text{pH} \approx 5,5$ a zinek i železo se rozpouštějí současně s rostoucím okyselením. Ustavení této pufrální rovnováhy souvisí s přítomností železa v nižších oxidačních stupních, zejména ve formě Fe(II).

Abstract

The forms of zinc in the blast furnace and steelmaking sludge were determined applying the sequential extraction method of chemical speciation. In the blast furnace sludge zinc is largely present in the ion-exchange and superficially occluded form and that is why its separation by acid leaching may be successful. These assumptions were proved when studying the heterogeneous acid-base equilibrium in discontinual static leaching under mild acidic conditions - $c(\text{HCl}) \text{ max. } 0.1 \text{ mol} \cdot \text{dm}^{-3}$, when 77 % of zinc were extracted and iron practically did not pass into solution.

As for the steelmaking sludge, an unambiguous correlation between the chemical speciation and acid leaching has not been found. When leaching this material, the buffering equilibrium is established at $\text{pH} \approx 5.5$ and both zinc and iron dissolve simultaneously with the growing acidification. This buffering equilibrium establishing is connected with the presence of iron in the lower oxidation states, especially in the Fe(II) form.

Key words: metallurgical wastes, chemical speciation, acid leaching

Introduction

Fine-grained metallurgical wastes are mostly stored in sludge lagoons. Metallurgical dusts and sludge contain 35 - 67 % of iron and a number of other metals in lower contents. That is why these wastes present a long-term potential risk of the environment contamination, above all the soil and both the surface and ground water contamination. It is useful to bring a maximum amount of the above metal containing wastes for both the economic and ecological reasons back into production. One of the ways how to solve the problem is the metallurgical wastes recycling, however, it is complicated considerably by the presence of undesirable elements, especially of zinc. The contents of this element in blast furnace and steelmaking sludge samples range from 0.5 to 6.0 % Zn. It is necessary to reduce the Zn content below 0.2 % before recycling. Taking into consideration different behaviour of zinc and iron at leaching by acids, hydrometallurgical methods could be suitable for reducing the Zn content.

Before processing it is necessary to get information about the compounds containing zinc as well as iron in a particular waste. Phase analysis methods (optical microscopy, X-ray diffraction, etc.) mostly used for that purpose do not have a sufficient trustworthy value for fine metallurgical wastes. It is caused by a considerable percentage of amorphous components in these materials and by too small dimensions of particles.

One of the methods enabling acquiring this information is a chemical speciation which is frequently used for contaminated soils, sediments, power station fly ash and flue dusts [1, 2]. The chemical speciation can be defined as a determination of concentrations of particular physicochemical forms of the element whose sum corresponds to the total element content in the sample. The metallurgical wastes evaluation by means of this method was published in refs. [3, 4].

The aim of the present work was to search for a relation between the Zn(II) chemical speciation in fine-grained metallurgical wastes and the acid leaching of zinc and iron occurring at certain acid-base equilibrium. This equilibrium is usually observed only in soil systems [5, 6]. Since the stored fine metallurgical waste is submitted in nature to the same processes as soils, the acid-base equilibrium can be utilized also for metallurgical emission study [3] and the behaviour of fine-grained metallurgical wastes at hydrometallurgical processing by acid leaching can be predicted from their conclusions.

1. Experimental

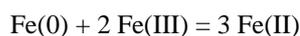
In the present work, the behaviour of two basic materials - blast furnace sludge (BFS) and oxygen converter sludge (OCS) - is compared. Contents of some components of the above wastes are shown in Table 1.

Table 1 Contents of some selected components in the blast furnace and steelmaking sludge samples (mass %)

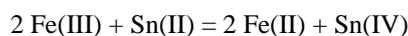
The AES-ICP method (JOBIN YVON 24 apparatus) was applied for determining the zinc content in leaches and the XRFS (EDS SPECTRO X-LAB) method for analysing solid samples. Particular forms of iron in original samples as well as in pure reference iron compounds were determined by the volumetric analysis methods in compliance with CSN 72 2041 standards, section 10 and 11 and ST SEV 4519 - 84.

All the three present forms of iron - Fe(0), Fe(II) and Fe(III) - were determined after their transformation into Fe(II) using the titration by potassium dichromate to ammonium diphenylaminsulfonate as an indicator.

Fe(0) is transformed into Fe(II) by the disproportionation reaction with FeCl₃



Fe(III) is reduced by tin dichloride in the acid medium



The iron present in the analysed sludge in the oxidation state II was also determined directly in the sample by means of bichromatometry after its dissolving in hydrochloric acid under the CO₂ atmosphere.

The behaviour of particular iron forms at acid leaching was verified using the following pure chemical compounds:

Fe metallic, p.a. Riedel-De Haën AG.Seelze, Hannover

FeO, p.a., Morton Thiokol, Inc., Alfa Products

Fe₂O₃, p.a Ventron Karlsruhe, Alfa Produkte

Fe₃O₄, p.a. Sigma Aldrich

The metallurgical wastes in question were also submitted to X-ray diffraction analysis which is, however, utilizable for the sample crystalline fraction only. Identification of zinc and the other heavy metals by means of this method is not possible because of their low contents. It is obvious from the phase analysis results (table 2) that FeO and Fe₂O₃ are present in the samples in the form of a separate phase as well as in the form of magnetite Fe₃O₄, i.e. FeO.Fe₂O₃.

Table 2 Phase composition of the crystalline forms of the blast furnace and steelmaking sludge samples

1.1 Chemical speciation

The zinc chemical speciation in fine metallurgical wastes was described in details in refs. [3, 4]. The method consists of seven basic steps in which more strongly bound fractions are gradually released from the leached material:

- step 1 - mobile fractions - water-soluble and exchangeable (non-specifically adsorbed) element forms and easily soluble organometallic complexes,
- step 2 - easily releasable fractions - specifically adsorbed, superficially occluded and CaCO₃ bound metals, organometallic complexes with weak bond strengths,
- step 3 - a fraction bound to manganese oxides,
- step 4 - an organically bound fraction,
- step 5 - a fraction bound to amorphous iron oxides,
- step 6 - a fraction bound to crystalline iron oxides,
- step 7 - a fraction bound to silicates and other resistant minerals.

The leached iron content was also determined in individual fractions.

1.2 Heterogeneous acid-base equilibrium

For studying heterogeneous acid-base equilibrium a discontinual static arrangement ("batch leaching") was opted in which a mixture of reactants was let quiet for certain time with occasional stirring only. Optimum leaching time for both the studied sludge types was determined on the base of the time dependencies of the studied elements extraction grade. This dependence was determined from the results of the series of measurements in which suspensions of samples and leaching acid were let in contact for various time periods under the entirely identical conditions. These experiments resulted in the conclusion that the maximum time required for establishing the equilibrium state in all the samples is 168 hours, i.e. seven days.

The static experiments themselves were performed under the following conditions:

Mass of sample 1 g.

Hydrochloric acid concentration in the range $c = 0 - 0.1$ mol/l.

Mass ratio of the leaching acid and solid sample $L/S = 100 : 1$.

Temperature 20°C .

When the material comes into contact with the leaching acid, the constituents soluble at the particular acid concentration are released and the buffering equilibrium is established. The dependence of the studied elements extraction on pH as well as the total element releasability from the material were determined from the series of measurements performed under the entirely identical conditions (sample amount, leaching solution volume, time, temperature) except the variable acid concentration.

2. Results and discussion

The results of the zinc chemical speciation in the blast furnace (BFS) and steelmaking (OCS) sludge are demonstrated graphically in figure 1. It is obvious from the figure that the zinc forms in both the compared materials are different. The blast furnace sludge contains about 77 % of extractable zinc and only about 10 % of this element remains in the matrix. On the other hand, only about 20 % of zinc were found in easily extractable forms (steps 1 and 2) in the oxygen converter sludge, while 63 % remain strongly bound in the matrix.

Fine-grained metallurgical materials contain considerable amounts of iron that can be extracted (leached) together with zinc, which can complicate the zinc removal from waste materials. This is the reason why it is also suitable to observe the iron amounts extracted in individual steps of the zinc chemical speciation and to estimate the iron behaviour at acid leaching of metallurgical sludge on the basis of the obtained results. The iron leaching at the zinc chemical speciation in the blast furnace (BFS) and steelmaking (OCS) sludge is shown figure 2.

It is obvious from the figure that though, from the chemical point of view, iron in both types of sludge is largely present in hardly extractable forms (steps 5 to 7), it was also extracted, to a certain extend, in earlier fractions from steelmaking sludge. We can conclude from these results that the easier soluble amorphous oxides of iron are present in steelmaking sludge (OCS) in the double amount than in blast furnace sludge (see step 5).

Fig.1 The chemical speciation of zinc in the blast furnace and steelmaking sludge

Fig.2 The iron content in individual steps of the chemical speciation of zinc in the blast furnace and steelmaking sludge

The heavy metals extractability determined by means of the chemical speciation can be verified by acid leaching. Heterogeneous acid-base equilibrium established in the course of this leaching enables to search for a correlation between the individual element extractability and their chemical speciation. For a better visual demonstration the graphs of chemical speciation and acid leaching for the same type of material are presented one below the other in figures 3 - 4 and 5 - 6.

In the process of the blast furnace sludge leaching (figure 4) the zinc release occurs at low concentrations of the used acid and a relatively high pH value. The extracted element amount corresponds to the amount of well extractable zinc forms determined by the speciation analysis of this type of waste - about 77 % in both cases. Iron does not practically dissolve and this fact is in a good accordance with the minimum amount of its easily extractable forms (figure 3).

Fig.3 Speciation analysis of the blast furnace sludge

Fig.4 Discontinual static leaching of the blast furnace sludge

The results obtained by the chemical speciation and acid leaching of the steelmaking sludge are compared in figures 5 and 6.

An unambiguous correlation between the chemical speciation and the sample acid leaching was found for steelmaking sludge. In this sludge the zinc dissolving at increasing acid concentration is connected with the iron dissolving and has no direct connection with the chemical speciation. It can be only estimated from the steelmaking sludge chemical speciation (figure 5) that about 60 % of Zn and 45 % of Fe bound in the matrix cannot be dissolved by acid leaching. The pH values established after reaching the equilibrium state when leaching by acid solutions differ considerably for the two types of waste in question (figures 4 and 6). In the steelmaking sludge the buffering equilibrium is established at $\text{pH} \approx 5.5$, while in the blast furnace sludge pH drops to the value corresponding to the used leaching acid concentration, i.e. around $\text{pH} = 1.0$.

Fig.5 Speciation analysis of the steelmaking sludge

Fig.6 Discontinual static leaching of the steelmaking sludge

The establishing of different equilibrium state pH values is related to different abundance of individual oxidation state of iron in the blast furnace and steelmaking sludge (table 1). These findings obtained at the acid leaching of fine-grained metallurgical wastes were proved by the heterogeneous acid-base equilibrium study of the defined iron compounds under the identical conditions. The pH values established in the oxidation-reduction reaction of Fe(s) with the acid are presented too [7]. The pH alteration when extracting these reference materials is shown in figure 7.

It is obvious from the figure that the buffering equilibrium of Fe(s) and FeO is established around $\text{pH} \approx 5$. FeO which is a part of magnetite Fe_3O_4 (table 2) does not dissolve in these low HCl concentrations and does not influence the pH value.

It is obvious from the comparison of the pH value dependence on the used acid concentration for pure materials (figure 7) and the steelmaking sludge in figure 6 that relatively high values of pH in the equilibrium state result from the presence of iron in the low oxidation states. The pH course when acidifying blast furnace sludge corresponds to the presence of iron in the oxidation state III and in hardly decomposable minerals (tab.1 and 2).

Fig.7 The dependence of pH on the form of present iron with increasing acid concentration

3. Conclusion

Fine-grained metallurgical wastes were characterized by means of the chemical speciation. It is obvious from the results that zinc is bound in a different way in both types of wastes. In blast furnace sludge zinc is present largely in easily extractable forms and we can suppose that its separation by leaching will be successful. Steelmaking sludge contains over 60 % of Zn strongly bound in the matrix and therefore it will be rather complicated to separate this metal applying hydrometallurgical procedures.

The results of discontinual static acid leaching of the blast furnace sludge showed that the zinc and iron leaching degree is in accordance with the chemical speciation results. The leaching of zinc from steelmaking sludge is influenced by the presence of iron in lower oxidation states because of its dissolving, which causes the buffering equilibrium establishing at $\text{pH} \approx 5.5$.

We can conclude from the behaviour of both types of sludge at gradual leaching that, with regard to the zinc higher extractability and lower iron extractability, blast furnace sludge will be especially suitable for hydrometallurgical processing of these materials.

Acknowledgements

The results of the project LN00B029 was supplied with subvention by The Ministry of Education of Czech Republic.

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