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Kinetic modeling of thermal decomposition of zinc ferrite from neutral leach residues based on stochastic geometric model

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ABSTRACT

The stochastic geometric model was applied to kinetic modeling the complex process of thermal decomposition of zinc ferrite from neutral leach residues, at different operating temperatures (600 °C, 750 °C, 950 °C and 1150 °C). Based on functional dependence of Avrami's constant (n) in a function of the effective activation energy (E_a), it was found that at $T > 950$ °C, the crystallization process takes place in autocatalytic stage, under the conditions where the rate of nucleation rapidly increases. It was established that the high nucleation rate can be attributed to formation of both Zn and Fe rich regions which provide a high number of heterogeneous nucleation sites. Based on the obtained final shape of the particles, it was found a strong presence of zinc, iron (present only in the form of Fe_3O_4 (magnetite)), magnesium (in the form of $Mg_2Si_2O_6$), and also lead oxides. Thermodynamic analysis showed that the decomposition depends on the introduction of heat, and exerts a positive value of the Gibbs free energy of activation. Such a feature was expected since the ferrite system has been submitted to a forced decomposition and volatilization reactions.

1. Introduction

Zinc is an important element especially for the steel industry and the formation of Electric Arc Furnace Dust (EAFD) leads to strong recycling activities. Zinc in primary fluidized bed calcine as well as in EAFD exists besides as simple oxides in a spinel form called zinc ferrite $ZnO \cdot Fe_2O_3$. A lot of studies have been conducted to find the most efficient way of zinc and iron recovery from the EAFD material due to environmental, technical and economical needs. Because of that there is a necessity for treatment of wastes containing zinc ferrites [1,2]. Different hydrometallurgical ways for recovering zinc from ferrite-phases exist such as acidic or caustic leaching, microwave assisted extraction, EZINEX process, etc. [3–5].

Leaching with sulfuric acid to obtain high recovery yield is feasible based on the following reaction:

$$ZnFe_2O_4 + 4H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Fe_2(SO_4)_3 + 4H_2O. \quad (1)$$

Eq. (1) can be expected even at room temperature, but the reaction rate is too slow. At the elevated temperatures and longer leaching time, significant extraction yields $> 80\%$ will occur, but the process is un-selectively decreased [6]. Zinc extraction becomes even higher if the solid/acid ratio is lowered. During this process, calcium sulfate precipitates resulting from low concentration of sulfuric acid and it remains until the end of process. Because of unselective leaching a yield of zinc is decreased [6]:

$$ZnFe_2O_4 + 2[OH^-] \rightarrow ZnO_2^{2-} + Fe_2O_3 + H_2O. \quad (2)$$

Other researches [5] have studied leaching kinetics of zinc ferrite in aqueous hydrochloric acid solutions according to reaction (3) and found that it is possible to precipitate ferric chloride, in the pH range of 3–4 and using air mixing:

$$ZnFe_2O_4 + 2HCl \rightarrow ZnCl_2 + Fe_2O_3 + H_2O \quad (3)$$

Their experiments have reached up to 90% zinc recovery under pH values between 3 and 4 at 90 °C. Unsuccessful experiments on ammonia leaching were conducted, where the EAF dust was firstly washed to solubilize the zinc oxide and then leached with ammonium chloride. But the zinc ferrite remains in residue. An organic acid process was also able to recover zinc from ferrite, when additional leaching step was introduced [5].

Today's commercial operations reach almost complete winning of zinc from zinc ferrite mostly are based on fuming operations that reduces ferrite and vaporizes zinc. Such pyrometallurgical applications use a reduction media such as carbon monoxide, hydrogen or coke [7].

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The carbothermic method [8] requires a minimum temperature of 800 °C and the partial pressure of zinc vapor which remains below 0.014 bar. A full reduction of EAF dust with hydrogen at lower temperatures produces both iron and zinc with double hydrogen requirement, compared to the selective reduction that only produces zinc [2]. The worldwide standard is thermal reductive treatment in the Waelz process [9] enabling strong destruction of the zinc ferrite whereby producing a slag with very limited probability for use and high energy input [10].

1.1. The main objective of the presented investigation

In last five years, the process development for high pressure and atmospheric leaching of electric arc furnace dust became a central part of research at the IME, RWTH Aachen University in Germany. For example, high pressure leaching revealed to be more effective from zinc extraction point of view, but not for iron [11]. Unfortunately, it was found that the high selectivity is obtained only with lower a/d ratios. In order to decompose zinc ferrite from neutral leach residues, a new experimental concept was developed and conceptually presented in Ref. [1].

In this paper, we present a theoretical concept to explain the detailed reaction mechanism of the isothermal decomposition of zinc ferrite from neutral leach residues, which, in itself, is a very complex physico-chemical process. The procedure was based on explanation of the process from the standpoint of the theory of the nucleation and growth of a new phase, presented as the stochastic geometric model (Johnson–Mehl and Avrami (JMA)) [12–15]. Actually, this approach involves the consideration of the process in the light of solid state phase transformation kinetics [16]. The kinetic consideration was supported by the proper thermodynamic (through the changes of thermodynamic functions) analysis [17]. This approach has an interesting potential for describing the decomposition kinetics of the considered system, when the system is subjected to the elevated temperatures under controlled experimental conditions. Mathematical modeling of such complex decomposition can be of crucial importance for the design, performance analysis, and further improvement of hydrometallurgical processes, which, as one of the major products provide separation of specific magnetic materials. This is very significant since that at the elevated operating temperature (above 1025 °C), solid solutions of both ferric and zinc oxides in zinc ferrite can be formed, and that, when heated to higher operating temperatures the dissolved ferric oxide lost oxygen, forming magnetite and the specimen became ferromagnetic. One of the main goals of the current investigation is to identify the factors affecting the kinetics of the overall decomposition process, where, as one of the products can expect the appearance of iron, in the form of magnetite.

2. Experimental

2.1. Material characterization

The zinc leach residue was obtained from former company Ruhr-Zink, Datteln, Germany, with a moisture content of 23%. Before the experimental investigation, the sample was dried at 120 °C overnight in order to eliminate the moisture presence. The Rietveld XRD (X-ray diffraction) analysis of an initial sample has shown the following chemical composition [in %]: 40.9 $ZnFe_2O_4$, 16.5 $CaSO_4$, 6.4 $MgSO_4$, 13.6 Zn_2SiO_4, 11.3 $PbSO_4$, 4.4 $KFe_3(SO_4)_2(OH)_6$, and 6.9 related to the other compounds. This phase change made materials more soluble and suitable for the leaching process, which was reported in our previously paper [1]. The gaseous phases of PbO and SO_2 were formed during thermal decomposition and removed with nitrogen as the carrier gas. At 1150 °C, the chemical composition of the final decomposed material amounted [in %]: 57.0 Fe_3O_4, 28.9 $Ca_2ZnSi_2O_7$, 8.4 ZnO, 5.0 Mg_2SiO_6 and 0.7 $ZnAl_2O_4$. A scanning electron microscope (model ZEISS DSM 982 Gemini) (SEM) was used for the characterization of the obtained particles. SEM images were used to study the surface morphology. For explanation the thermo-chemical prediction of the formed products, the FactSage® thermochemical software with databases [18] was used.

2.2. The isothermal measurements

After 15 min of heating the samples in order to eliminate the contained moisture, these were used in the thermal treatment experiments performed in the tube furnace. At the fixed operating temperatures (600, 750, 950, 1150 °C), four experiments were performed at each operating temperature in the certain time intervals (15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 min). The experiments were repeated three times. After reaching the aimed temperature, 1 g of the zinc leach residue was inserted in a tubular furnace, under a constant nitrogen gas, with a flow rate of $\varphi = 1\ \mathrm{L\ min^{-1}}$. After beginning of the thermal treatment of dried sample at the fixed operating temperature, the reaction time was measured by chronometer (in digits form). After that, the specimen was taken out from the furnace and placed in the exiccator. The weight results were noted as an average mass lost of the specimen, in order to calculate the decomposition rate.

The conversion fraction (α) in the isothermal measurement at the considered operating temperature T is calculated by the following equation:

$$\alpha = \frac{m_{o(15)} - m_t}{m_{o(15)} - m_f} \tag{4}$$

where $m_{o(15)}$ is the initial mass of the sample (for time at $t = 15$ min, after removing of any remaining moisture at a given temperature (the time period from $t = 0$ min to $t = 15$ min at each of the considered operating temperature T, corresponds to time scale where the removal was done for possible residual moisture)), m_t is the mass of the sample at time t, and m_f is the final constant mass of the sample, after the establishment of the saturation (the saturation involves reaching the conversion value of $\alpha = 1.00$). Thus, the conversion data are calculated for completely dry samples at each of the observed temperatures. The decomposition of zinc leach residue in an inert atmosphere at every considered operating temperature begins after the 15th minute.

3. Theoretical background

Most solid state transformations do not occur instantaneously because obstacles impede the course of the reaction and make it dependent on time. For example, since most transformations involve the formation of at least one new phase that has a composition and/or crystal structure different from that of the parent one's, some atomic rearrangements via diffusion are required. A second impediment to the formation of a new phase is the increase in energy associated with the phase boundaries that are created between parent and product phases. From a microstructural standpoint, the first process to accompany a phase transformation is nucleation – the formation of very small (often submicroscopic) particles, or nuclei, of the new phase, which are capable of growing. Favorable positions for the formation of these nuclei are imperfection sites, especially grain boundaries. The second stage is growth, in which the nuclei increase in size. During this process, some volume of the parent phase disappears. The transformation reaches completion if growth of these new phase