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Kinetics of sulfuric acid leaching of cadmium from Cd–Ni zinc plant residues

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ABSTRACT

Cd–Ni filtercakes are produced continuously at the third purification step in the electrolytic production of zinc in the National Iranian Lead and Zinc Company (NILZ) in northwestern Iran. In this research, the dissolution kinetics of cadmium from Cd–Ni residues produced in NILZ plant has been investigated. Hence, the effects of temperature, sulfuric acid concentration, particle size and stirring speed on the kinetics of cadmium dissolution in sulfuric acid were studied. The dissolution kinetics at 25–55 °C and $t \leq 5$ min was found to follow a shrinking core model, with inter-diffusion of cadmium and sulfate ions through the porous region of alloying layer (Cd_5Ni, $Cd_2Ni_{1.9}$ and $Cd_{10}Cu_3$) as the rate determining step. This finding is in accordance with the apparent activation energy (E_a) of 13.363 kJ/mol and a linear relationship between the rate constant and the reciprocal of squared particle size. Arrhenius constant was calculated as 6.3942 min^{-1}. The order of reaction with respect to sulfuric acid concentration, solid/liquid ratio and particle size were also achieved. The rate of reaction at first 5 min based on diffusion-controlled process can be expressed by a semi-empirical equation as:

$$\left[1-\left(\frac{2}{3}\right)X-(1-X)^{2/3}\right]=k_d t=997[H_2SO_4]^{1.0475}\left(\frac{S}{L}\right)^{-0.5969} r_0^{-2.1819}\exp\left(-\frac{13.363}{RT}\right)t$$

It was determined that the dissolution rate increased with increasing sulfuric acid concentration and decreasing particle size.

"*It's a very funny thought that if bears were bees, they'd build their nest at the bottom of trees, and that being so (if bees were bears), we shouldn't have to climb up all those stairs.*"
From Winnie-the-Pooh, By A.A. Milne

1. Introduction

In spite of their toxicity, cadmium and its compounds are used in different industries such as electroplating, pigments, synthetic chemicals, ceramics, metallurgical and photographic products, electronics and other industries. Industrial applications for cadmium have recently been developed and consequently the direct production of this metal has increased [1].

Located in northwestern province of Zanjan, Iran, in NILZ electrolytic zinc plant, with a capacity of 20,000 t Zn/y, a major amount of Cd–Ni filtercake has been stockpiled during the years and also about 50 kg of the same residue per ton of produced zinc is added to dumps daily.

Fig. 1 shows a conceptual flow sheet which explains the purification stages and origin of the Cd–Ni filtercake in NILZ plant.

The following items draw our attention to treat Cd–Ni residues:

1. stringent environmental rules;
2. increasing demand for cadmium metal;
3. easy and fast dissolution kinetics of the residue in sulfuric acid;
4. increasing prices of cadmium [2].

Depending on the composition of zinc concentrate, the composition of filtercake may vary. For example, the average composition of such a filter cake in Iranian zinc plants is as follows [2]:

$$Zn = 40\text{–}55\%;\ Cd = 13\text{–}16\%;\ Ni = 3.5\text{–}4.0\%;$$

$$Cu = 1.5\text{–}2.0\%;\ Pb = 1.0\text{–}1.5\%;\ Ca = 2\text{–}3\%.$$

The high nickel content of this residue has made it different from similar residues produced in other zinc plants. As a result, the

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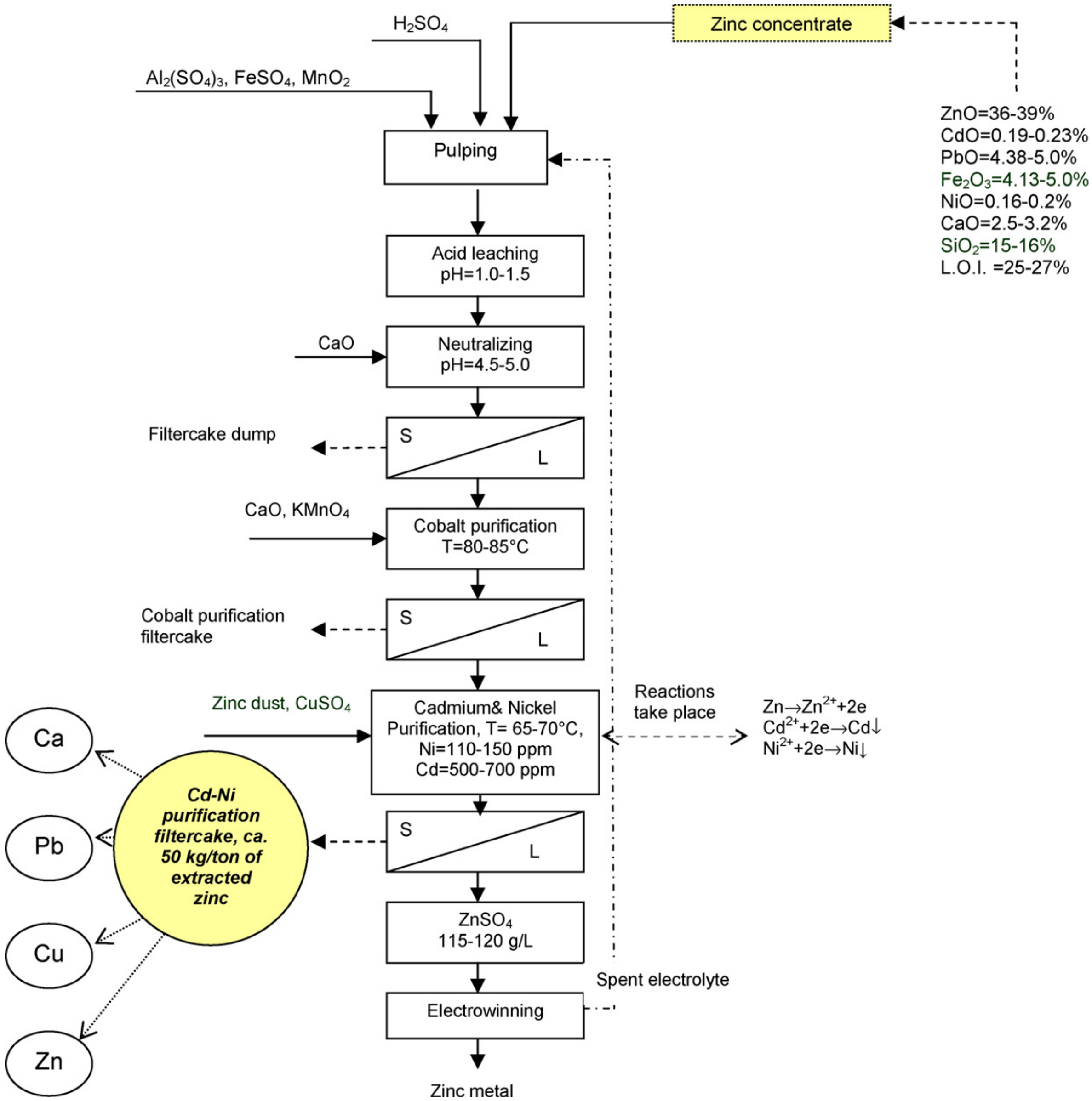

Fig. 1. Conceptual flowsheet of electrolytic zinc production in NILZ plant showing the origin of Cd–Ni purification filtercake [2].

appropriate treatment for this residue has become important from hydrometallurgical and economical points of view [3].

It might be useful to review the process in which Cd–Ni is attained. As seen in Fig. 1, the Cd–Ni filtercake is produced through cementation of impurities which accompany zinc sulfate solution using zinc powder and as a result all impurities are reduced on zinc particles. The reaction that occurs, however with excess of zinc much higher than the stoichiometric amount needed. The cementation reaction is a galvanic one in nature, therefore not only cadmium, nickel and copper are cemented on zinc, but also copper and nickel can cement on cadmium. Therefore it is expected that some other metallic compounds be present in the residue which will affect the subsequent leaching process in order to recover the metals [2].

To the best of our knowledge, no experimental report exists on the leaching kinetics of Cd–Ni filtercake in the relevant literature. Safarzadeh et al. [4] have determined the optimum conditions for the leaching of Cd–Ni zinc plant residues using Taguchi experimental plan, with no kinetic evaluation. In this paper, we aim the dissolution behavior of cadmium in sulfuric acid and also seek a kinetic model to explain its leaching rate.

In this research, the results of leaching of Cd–Ni filtercake with sulfuric acid are presented. The kinetics characterizations of the leaching process were analyzed according to shrinking core model (SCM) [5] and the best fitted equation to the experimental data was determined. A corresponding diffusion model was found suitable to explain the relationship between reaction time and the fraction of cadmium leached and the apparent activation energy of the process was determined. In the leaching experiments, the effects of temperature, acid concentration, stirring speed and solid/liquid ratio on cadmium extraction were investigated.

2. Chemistry of the solution and theoretical behavior of the phases

The leaching of Cd–Ni zinc plant residues deals with the solubilization of Zn, Cd, Ni, Cu and Pb in the form of oxides or elements, present in the filtercake. The behavior of these solid phases under