ABSTRACT

The removal of copper and lead ions from aqueous solutions by sorption on electric furnace slag (EFS) has been investigated. Experiments were performed at three temperatures of 23, 40 and 55 °C. The results of sorption kinetics are tested by kinetic model that describes intraparticle diffusion, and diffusion coefficients have been calculated. Diffusion rate of both systems increases with temperature, in dependence of time is constant for copper ions, while for lead decreases. The values of diffusion coefficients depend of hydrated radius of ions and pH values in the suspensions.

Keywords: copper, lead, electric furnace slag

1. INTRODUCTION

Production of steel and cast steel in an electric arc furnace is increasing therefore an increasing attention is being paid to electric furnace slag, which is generated in quantity of 15% per ton of steel. The European countries in year 2004 were generated ≈15 000 000 t of solid material in steel processing, where portion of electric furnace slag was 29 %, i.e. 4 350 000 t [1]. Due to its properties the electric furnace slag is non-toxic waste material that has to be disposed on the specially arranged depots. This process is rarely applied, it is expensive, requires a lot of area and there is a danger of possible leaching of solid waste material. The produced leachate is new liquid waste that becomes additional environmental pollution. Therefore, it is indispensably needed to analyse this metallurgical waste material and in accordance with the results, to use it as a valuable secondary raw material. The earliest reports on the use of slags referee the Aristotle who used slag as a medicament as early as 350 B.C. During the passed two centuries the slag mainly has been used as construction material. More applications have been developed in last century, e.g. use of electric furnace slag as fertiliser, binding agent and/or addition for concrete, replacement for certain mineral raw materials in production of glass and glass wool, for sorption metal ions in waste water purification processes etc. [1-4].

In this paper are presented the examination of removal copper and lead ions from aqueous solutions by sorption on electric furnace slag (EFS) performed in the foundry "Felis produkti" d.o.o. based in Sisak.
2. EXPERIMENTAL

The chemical composition of electric furnace slag was determined by the standard chemical analysis and results in mass % are CaO-30 %; MgO-0.2 %; MnO-19 %; SiO\textsubscript{2}-19 %; Al\textsubscript{2}O\textsubscript{3}-1.3 %, FeO-30 %.

All experiments have been made with a granulometric fraction of 0.05 to 0.70 mm.

Examination of removal of Cu and Pb ions from aqueous solutions on EFS were performed by batch method by shaking of 0.2000 g of EFS with 50.00 mL of Cu and Pb ions solution with initial mass concentration of 250 mg/L. The three series of suspensions were examined, each at different temperature of 23, 40 and 55°C. At each temperature, shaking of suspensions was interrupted at different contact time (0 - 1440 min) and the suspensions were filtered. The concentrations of copper and lead ions remained in the liquid phase were determined using atomic absorption spectrometer (Shimadzu, AA 6800). The pH values in suspensions before and after experiments were measured using pH-meter.

3. RESULTS AND DISCUSSION

The experimental results of concentrations obtained from examination of sorption kinetics at different temperatures are presented as amount of copper and lead bound per unit mass of electric furnace slag (EFS) and given on figure 1.

![Figure 1. The amount of a) copper and b) lead ions, bounded vs. time at different temperatures.](image-url)

From the figure 1 is clear that removal of copper and lead ions by electric furnace slag is a slow process, favored with increasing of temperature. Compared to copper the removal of lead is some faster at initial times of experiment, with higher quantity of lead bounded per unit mass of EFS. Equilibration in both examined systems is achieved at approximately 1000 minutes. The high time interval needed for equilibration between solid and liquid phase indicates that adsorption of ions is dominate mechanism responsible for removal of Cu and Pb in these suspensions. The experimental results shown on the figure 1, have been tested with kinetic model that describes diffusion through porous solid particle. This model is named the homogeneous diffusion model and evaluated from the second Fick’s law with the assumption that diffusion rate and radial diffusion coefficient is constant during ion exchange process, and expressed as [5,6]:

\[
F = 1 - \sum_{i=0}^{\infty} a_i \exp\left(-b_i t / \tau\right)
\]

where

\[
F = \frac{q_t}{q_e}
\]

\(F\) = fraction of metal ion bound at time \(t\)

\(q_t\) = mmol of metal ion per g of EFS in time \(t\)

\(q_e\) = mmol of metal ion per g of EFS at equilibrium
\( i \) = number of experimental points.

\( a_i \) and \( b_i \) are parameters that depend on the shape of the solid particle, and \( \tau \) is the time needed for diffusion of the metal ion from the particle surface to the sorption site in the particle and equals:

\[
\tau = \frac{r^2}{D}.
\]

For sphere particles, equation (1) can be rewritten in a form that reduces at large \( t \) to:

\[
t \rightarrow \infty, \quad \ln(1-F) = \ln \left( \frac{6}{\pi^2} \right) - \pi^2 D t. \tag{4}
\]

From graphical dependence of Cu or Pb bounded vs. time the diffusion coefficients have been calculated from the slope of the linear part of curves given by equation (4), (Figure 2).

For copper ions the model gives linear dependences in all time interval and for all examined temperatures (Figure 2a). These lines have similar slope that means close values of intraparticle diffusion coefficients what indicates constancy of diffusion rate and mass transfer mechanism. Compared to copper ions, sorption of lead gives curves with inflection point that separate each curve into two areas (Figure 2b). At these areas the plots approach linearity, so that linearization of the curves was performed at two time intervals; first at 0-200 min and second from 200 min to the equilibrium. The diffusion coefficients have been calculated for each time interval and temperature, and given in table 1.

**Table 1. Diffusion and correlation coefficients for sorption of Cu and Pb on EFS.**

<table>
<thead>
<tr>
<th>temperature</th>
<th>( 23^\circ \text{C} )</th>
<th>( 40^\circ \text{C} )</th>
<th>( 50^\circ \text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu</strong> D ( \times 10^{-7} ), cm(^2)/min</td>
<td>0.677</td>
<td>0.784</td>
<td>0.963</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.96</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td><strong>Pb</strong> D ( \times 10^{-7} ), cm(^2)/min</td>
<td>0.891</td>
<td>2.246</td>
<td>2.532</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.97</td>
<td>0.97</td>
<td>0.94</td>
</tr>
<tr>
<td>0-200 min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 min to eq. D ( \times 10^{-7} ), cm(^2)/min</td>
<td>0.214</td>
<td>0.249</td>
<td>0.428</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.94</td>
<td>0.95</td>
<td>0.96</td>
</tr>
</tbody>
</table>

From table 1 is clear that diffusion coefficients as well as diffusion rate increases with increased temperature. The diffusion rate for copper ions is constant, while diffusion rate of lead ions changes vs. time what indicate changes is sorption mechanism. The values of diffusion coefficients shows that sorption of lead at the initial time is faster compared to copper ions. This can be attributed to radius of hydrated lead ions that is lower compared to copper ions. The pH values in system of lead-EFS is some higher (5.82-6.40) than in system copper-EFS (5.14-5.90). At pH=6 the hydrolysis of Pb\(^{2+}\) ions.
occurs that contributes to formation of monovalent Pb(OH)$^+$ specie with lower radius of hydrated ion [7]. This ion has better mobility through porous solid structure, and occupies one sorption site, what explains some higher sorption capacity of EFS for lead ions.

4. REFERENCES


5. ACKNOWLEDGMENT

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