Cementation Extraction of Lead from Sulphate Cake

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Abstract

Results of investigation of the process of lead cementation from its sulphate on powdered metals, namely, zinc dust and iron powder, under dynamic and static conditions have been presented. It has been demonstrated that the process runs more intensively without stirring. Kinetic characteristics of the process have been determined.

INTRODUCTION

In cementation the replacement of one metal by another occurs, and the former (the cemented metal) passes from ionic condition to metallic one, whereas the second (the cementing metal) passes from metallic to ionic form. This process often is also spoken of as "contact replacement" [1]. Generally, the reaction that underlies the process is described by the equation

$$a\mathrm{Me}_1^{b+} + b\mathrm{Me}_2 = a\mathrm{Me}_1 + b\mathrm{Me}_2^{a+} \quad (1)$$

where Me_1 and Me_2 are the cemented and cementing metals respectively; a and b are the valences of the metals.

Reaction of cementation proceeds provided that it is accompanied by a decrease of the thermodynamic potential. This is the case if a cementing metal possesses a more negative electrochemical potential than the cemented metal. If cementation is not accompanied by the formation of an alloy or a chemical compound, then the equilibrium condition may be written as

$$\varphi^{\mathrm{o}}_{\mathrm{Me}_1} + [RT/(z_1F)]\ln a^{z_1+}_{\mathrm{Me}_1} = \varphi^{\mathrm{o}}_{\mathrm{Me}_2} + [RT/(z_2F)]\ln a^{z_2+}_{\mathrm{Me}_2} \quad (2)$$

where $\varphi^{\mathrm{o}}_{\mathrm{Me}_1}$ and $\varphi^{\mathrm{o}}_{\mathrm{Me}_2}$ are standard potentials of the cemented and cementing metals respectively; $a^{z_1}_{\mathrm{Me}_1}$ and $a^{z_2}_{\mathrm{Me}_2}$ are the activities of their ions in the solution; R is universal gas constant; F is Faraday constant; T is the absolute temperature.

From the given equation it follows that the ratio of the activities $a^{z_1+}_{\mathrm{Me}_1}/a^{z_2+}_{\mathrm{Me}_2}$ in the solution in an equilibrium state is expressed by the equation

$$a^{1/z_1}_{\mathrm{Me}_1}/a^{1/z_2}_{\mathrm{Me}_2} = \exp[(\varphi^{\mathrm{o}}_{\mathrm{Me}_2} - \varphi^{\mathrm{o}}_{\mathrm{Me}_1})F/(RT)] \quad (3)$$

Table 1 gives the results of computations of an equilibrium condition according to this equation under standard conditions for certain pairs of metals. Here, it is supposed that iron is oxidized to bivalent state.

As suggested by the evidence presented, lead can be isolated through cementation on zinc, iron, and aluminium even from such difficultly soluble compounds as sulphate, carbonate or hydroxide, whose solubility calculated based on their solubility products [2] comprises $1.26 \cdot 10^{-4}$, $2.74 \cdot 10^{-7}$ and $2.22 \cdot 10^{-7}$ mol/dm^3, respectively.

The work [3] recommends one to use cementation of lead from its sulphate on zinc plates in sodium chloride solution to obtain a spongy metal. However, owing to a small area of contact between the reactants, the reaction rate is small; therefore it cannot be recommended in this version for industrial use. The purpose of this work is searching for ways to increase the efficiency of the cementation process when obtaining lead from sulphate cakes with a prospect for its industrial use.

TABLE 1

Electrode potentials and the ratios of equilibrium activities for certain pairs of metals calculated based on the equation (3)

Metal		Standard potential, V [2]		$a_{Me_1}^{z_1+} / a_{Me_2}^{z_2+}$
Cemented	Cementing	Cemented metal	Cementing metal	
Lead	Zinc	−0.126	−0.763	$1.65 \cdot 10^{-11}$
«	Iron	−0.126	−0.440	$4.85 \cdot 10^{-6}$
«	Cadmium	−0.126	−0.402	$2.13 \cdot 10^{-5}$
«	Aluminium	−0.126	−1.670	$7.41 \cdot 10^{-27}$
Cadmium	Zinc	−0.402	−0.763	$3.2 \cdot 10^{-13}$
«	Iron	−0.402	−0.440	$5.2 \cdot 10^{-2}$
Iron	Zinc	−0.440	−0.763	$8.0 \cdot 10^{-27}$
Copper	«	+0.340	−0.763	$1.00 \cdot 10^{-38}$
«	Aluminium	+0.340	−1.670	$9.63 \cdot 10^{-35}$
«	Iron	+0.340	−0.440	$3.61 \cdot 10^{-27}$
«	Nickel	+0.340	−0.230	$2.0 \cdot 10^{-20}$
Mercury	Copper	+0.738	+0.340	$1.6 \cdot 10^{-16}$

EXPERIMENTAL

The possibility for use of powdered metals with much greater specific surface, namely, zinc dust and iron powder, as cementing agents has been investigated with the aim of accelerating the reaction. Study of the effect of various factors on the degree of advancement of cementation process was performed by the following procedure: a starting material (reagent-grade lead sulphate) and a powder of cementing metal were mixed by following a stoichiometric course in beakers (the ratio of liquid and solid phases was equal to 8 : 1). The obtained mixture was held at a constant temperature that was maintained by means of a thermostat with an accuracy of ±0.5 °C during a specified time. Thereafter the reaction products were elutriated, separated from each other by means of filtration, and the main components were then determined.

Originally (based on general regularities of heterogeneous chemical reactions) the cementation was conducted with stirring the reaction mixture that occurred by means of glass propeller stirrers. In so doing the temperature dependence of the degree of advancement of the reaction in the interval 293–353 K has been investigated. The duration of the experiments in all cases comprised 6 h. Results of the experiments are presented in Table 2.

RESULTS AND DISCUSSION

As shown by the findings lead extraction degree into lead sponge does not reach the values that are acceptable for practical purposes and it comprises 35 % when zinc dust is used and about 40 % when used iron powder. In addition, the lead sponge that was received during cementation contains a significant

TABLE 2

The action of temperature on the degree of lead extraction from sulphate into lead sponge when stirring the pulp

Temperature, K (°C)	Cementing metal		Extraction degree, %
293 (20)	Zinc dust		3.8
313 (40)	«	«	4.4
323 (50)	«	«	12.0
333 (60)	«	«	20.50
343 (70)	«	«	22.0
353 (80)	«	«	22.25
303 (30)	Iron powder		35.0
318 (45)	«	«	37.0
333 (60)	«	«	37.0
353 (80)	«	«	39.2

TABLE 3

Temperature effect on lead extraction degree from sulphate into lead sponge by cementation without stirring the reaction mixture (under static conditions)

Process temperature, K (°C)	Cementing metal		Degree of extraction, %
293 (20)	Zinc dust		70.5
313 (40)	«	«	82.0
323 (50)	«	«	89.2
333 (60)	«	«	90.0
343 (70)	«	«	93.0
353 (80)	«	«	100.0
303 (30)	Iron powder		76.8
315 (45)	«	«	88.0
333 (60)	«	«	90.0
353 (80)	«	«	91.3

amount of unreacted cementing metal. Owing to high plasticity of lead, dense granules are formed on pelletizing. The rate of diffusion of lead ions towards the surface of cementing metal therewith drops sharply and stopping of the process occurs.

Friction of metallic grains and lead sulphate on stirring facilitates pelletizing with all the consequences that follow from it. The assumption has been made that agitation has a negative influence on the extraction of lead. Therefore we have carried out a series of experiments on cementation without resort to stirring. With this aim in view, dry starting materials were mixed with each other, and then the received mixture was covered with water in such a way as to prevent stirring-up. Otherwise the procedure was the same. Results are presented in Table 3. It is evident that the freedom from stirring has

TABLE 4

Variation of the degree of advancement of the reaction of lead cementation from its sulphate on zinc dust as a function of the process duration

Duration of the experiment, s (min)	Degree of advancement of the reaction, %
Temperature 313 K	
1800 (30)	41.42
3600 (60)	42.3
7200 (120)	70.05
10800 (180)	73.70
14400 (240)	76.68
21600 (360)	86.62
25200 (420)	92.84
Temperature 333 K	
1800 (30)	42.80
3600 (60)	53.26
7200 (120)	77.28
10800 (180)	84.20
14400 (240)	89.51
Temperature 353 K	
1800 (30)	41.66
3600 (60)	74.56
9000 (150)	87.07
10800 (180)	87.70
14400 (240)	98.19
25200 (420)	98.51

TABLE 5

Variation of the degree of advancement of the reaction of lead cementation on iron powder as a function of the process duration

Duration of the experiment, s (min)	Degree of advancement of the reaction, %
Temperature 313 K	
1800 (30)	41.42
3600 (60)	42.30
7200 (120)	70.05
10800 (180)	73.70
14400 (240)	76.68
21600 (360)	86.62
25200 (420)	88.00
Temperature 333 K	
1800 (30)	42.80
3600 (60)	53.26
7200 (120)	77.28
10800 (180)	84.20
14400 (240)	89.51
25200 (420)	90.52
Temperature 353 K	
1800 (30)	41.66
3600 (60)	74.56
9000 (150)	87.07
10800 (180)	87.70
14400 (240)	91.30
25200 (420)	92.24

TABLE 6

Results of processing the experimental data on lead cementation from its sulphate by Kolmogorov–Erofeev and Sakovich equations

Temperature, K (°C)	Constants in the Kolmogorov–Erofeev equation [4]		Reaction rate conctant calculated by Sakovich equation [5]
	n	K	
Cementing metal is zinc dust			
313 (40)	0.615	$4.57 \cdot 10^{-3}$	$9.638 \cdot 10^{-5}$
333 (60)	0.607	$5.92 \cdot 10^{-3}$	$1.303 \cdot 10^{-4}$
353 (80)	0.686	$5.34 \cdot 10^{-3}$	$3.353 \cdot 10^{-4}$
Cementing metal is iron powder			
313 (40)	0.568	$6.695 \cdot 10^{-3}$	$8.512 \cdot 10^{-5}$
333 (60)	0.608	$6.943 \cdot 10^{-3}$	$1.329 \cdot 10^{-4}$
353 (80)	0.572	$9.715 \cdot 10^{-3}$	$1.745 \cdot 10^{-4}$

a positive effect on the extraction of lead, especially at elevated temperatures.

In addition, as follows from data of Table 3, somewhat better indices are achieved when zinc dust is used as cementing metal than are with iron powder. This is in a good agreement with the fact that activity of zinc is higher relative to iron.

With the aim of determination of kinetic characteristics of the process, the dependence of extraction degree of lead into lead sponge on the duration of the process has been studied at the temperatures of 313, 333, and 353 K (40, 60, and 80 °C). All experiments have been conducted under identical conditions that eliminate stirring. Results of the experiments are presented in Tables 4 and 5.

As a result of processing the experimental data by Kolmogorov–Erofeev and Sakovich equations (Table 6), it has been demonstrated that reaction of cementation proceeds in the diffusion field. From general regularities one might assume that diffusion of ions of metals through the layer of the formed lead sponge is the limiting stage. At the same time, a small variation in coefficient n with temperature in Kolmogorov–Erofeev equation demonstrates that the quantity of reaction centres in the mixture varies slightly with increase in reaction temperature.

CONCLUSIONS

It has been found experimentally that stirring of the pulp has a negative effect on the process of lead cementation from its sulphate on powder cementing agents: zinc dust and powder iron. The maximum extraction degree of lead into sponge amounts to 22.25 % at 80 °C and when employing zinc dust as a cementing agent, and that with powder iron is 39.2 %. For cementation in static conditions (without stirring the pulp) with prior dry mixing of lead sulphate with zinc dust as a cementing agent, the extraction degree of lead into sponge amounts to 100 %, and that with iron powder is 91.3 %. It has been demonstrated that reaction of cementation is controlled by diffusion of ions of metals through the layer of formed lead sponge. The temperature slightly influences the rate of the process.

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