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COMPARISON OF SELECTED METHODS OF INDUSTRIAL MAGNESIUM SULPHATE PURIFICATION FROM IRON COMPOUNDS

PORÓWNANIE WYBRANYCH METOD OCZYSZCZANIA PRZEMYSŁOWEGO SIARCZANU MAGNEZU ZE ZWIĄZKÓW ŻELAZA

Abstract

This paper presents the results of industrial magnesium sulphate purification from iron compounds. Purification of industrial magnesium sulphate was conducted by means of two methods. The first method consisted in adding sodium hydroxide solution until the desired pH was reached. At the desired pH value iron compounds were precipitated in the form of insoluble iron (III) hydroxide. The second method consisted in obtaining sodium, potassium and ammonium jarosite. Precipitation of jarosite resulted from the addition of potassium sulphate, sodium sulphate or ammonium sulphate. After the addition of selected sulphate salt agent sulphuric acid solution was added in order to achieve appropriate pH value. Jarosite was formed at elevated temperature only. Precipitation process was conducted with different reactants concentrations and under varying stoichiometric conditions. High degrees of Fe(III) ions removal from tested solutions amounted to 100%.

Keywords: magnesium sulphate, jarosite

Streszczenie

W artykule zaprezentowano wyniki oczyszczania przemysłowego siarczanu magnezu ze związków żelaza. Oczyszczanie prowadzono z zastosowaniem dwóch metod. Pierwsza metoda polegała na dodatku roztworu wodorotlenku sodu aż do osiągnięcia odpowiedniej wartości pH, przy której następował strącanie osadu w postaci wodorotlenku żelaza (III). Druga metoda polegała na strącaniu jarosytu sodowego, potasowego oraz amonowego. Strącanie jarosytu następowało w skutek dodatku siarczanu potasu, siarczanu sodu lub siarczanu amonu. Po dodatku czynnika odpowiedniej soli siarczanowej, dodawano roztwór kwasu siarkowego w celu osiągnięcia odpowiedniej wartości pH. Jarosyt powstawał dopiero w podwyższonej temperaturze. Proces strącania prowadzono przy różnych stężeniach reagentów oraz w różnych warunkach stochiometrycznych. Osiągnięto wysokie stopnie usunięcia żelaza rzędu 100%.

Słowa kluczowe: siarczan magnezu, jarosyt

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1. Introduction

The basic raw material for the preparation of magnesium sulphate is magnesite. In addition, more and more recyclable materials are used to obtain this product [1, 2].

An example of such a technology is the technology of obtaining electrolytic zinc from zinc ores by means of enrichment and chemical processing. Magnesium sulphate is derived from both the removal of magnesium from zinc concentrate and from the residues of the electrolyte obtained by electrolytic zinc. The obtained magnesium sulphate is the waste product characterized by the increased contents of zinc, lead, calcium and iron compounds. After the initial treatment, magnesium sulphate may become a commercial product which does contain small amounts of the aforementioned compounds. Therefore, it is mostly used in fertilizers, and the desired concentrations of zinc and iron compounds are considered micronutrients [3,4]. Magnesium sulphate is a suitable material for the preparation of magnesium hydroxide with controlled physicochemical properties. However, in this case it must be characterized by high purity and therefore requires further purification, mainly from iron compounds. Purification may be carried out in various ways, the most popular one is the method of precipitation. These methods make use of sparingly soluble metal compounds, further separated by filtration. Purification technology solutions for the production of non-ferrous metals are provided by the following methods.

Table 1
Methods used to remove iron compounds

Process	Precipitation	Residue [t/t ore]	Residue composition [%]		
			Fe	Zn	S
Jarosite	MFe ₃ (SO ₄) ₂ (OH) ₆	0.40	25–30	4–6	10–12
Goethite	FeOOH	0.25	40–45	5–10	2.5–5
Hematite	Fe ₂ O ₃	0.18	50–60	0.5–1	2–3

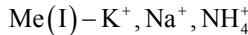
- Selecting one of these methods depends on many factors such as:
- investment costs,
 - operating costs,
 - quantity of waste generated,
 - the ability to filter,
 - the possibility of using the waste generated as secondary raw materials in other processes,
 - degree of risk to the environment [5].

In practice, the method using jarosite is the most common one because of its techno-economic performance (good filterability of sludge, the possibility of removal in acidic environment, low cost, etc.).

The following is the process equation (1)



where:



Depending on the salt used Me(I) is given an appropriate form of jarosite. The analysis of a thermodynamic temperature range of 323–373K shows that potassium jarosite forms within the whole temperature range in contrast to sodium jarosite, which occurs at over 353 K. For example, the logarithm of the equilibrium constant for 353 K for sodium jarosite is 0.06, while for potassium jarosite 5.432. These constants at 373 K take the values of 2.239 and 5.914, respectively. These data show that the removal efficiency of Fe(III) is greater in the presence of potassium ions [6].

Other methods used to remove unwanted metals are ion exchange resins. However, they have a lot of limitations due to the necessity of using very dilute solutions.

2. Experiment

Purification of industrial magnesium sulphate with high content of iron was performed by precipitation and the jarosite method.

In the precipitation method a material is introduced to the solution, then hydrogen peroxide is added (to oxidize Fe^{2+} to Fe^{3+}) as well as 0.1 M NaOH while stirring. Dosing of sodium hydroxide was performed until the appropriate pH value was reached, and its low concentration was reduced by the co-precipitation of magnesium hydroxide. The precipitation process was performed at ambient temperature. In order to determine the impact of the initial concentration of magnesium sulphate solution, the cleaning solutions of the following concentrations were introduced: 2.2, 2.0, 1.8, 1.6, 1.4 [mol/dm³]. After the purification process the precipitation mixture was separated on a sand filter, and the final filtrate was concentrated to the crystallization of magnesium sulphate heptahydrate. The composition of industrial magnesium sulphate before treatment is summarized in Tab. 2.

Table 2

Particular component content in industrial MgSO_4

Concentration of metals in industrial MgSO_4				
Mg ²⁺ [%]	Na [%]	Fe [ppm]	Zn [ppm]	total H ₂ O [%]
13.98	0.66	43	26	28.46

The second method – the jarosite method – consisted in adding to the solution of magnesium sulphate appropriate industrial salts: potassium sulphate jarosite to obtain potassium jarosite, sodium sulphate to obtain sodium jarosite and ammonium sulphate in order to obtain ammonium jarosite. Precipitation was performed in a boiling solution. The initial concentrations of magnesium sulphate solution used for the jarosite method was the

same as in the case of the precipitation method. For the purpose of lowering the pH, dilute sulphuric acid in 1:5 ratio (acid part/water part) was used. After the process was finished, the precipitation mixture was separated on a sand filter and the filtrate was subjected to the crystallization concentration of magnesium sulphate heptahydrate.

The content of magnesium and iron in both the solution and the sediment was determined by spectrophotometry.

3. Results and discussion

Tab. 3 presents the mass balance of the purification process by the precipitation method in relation to 1.00 dm³ purified solution of a suitable concentration. The values in the table are average of the three values obtained for the three tests in parallel. Precipitation was carried out in order to achieve a pH of about 9.4–9.6.

Table 3
Mass balance of the purification process by precipitation method

$MgSO_4$ initial con- centration [mol/dm ³]	Concentration of magnesium and iron ion [g, mg]						Degree of Fe removal [%]	Loss of Mg [%]		
	before purification		after purification							
	solution		solution		precipitate					
	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]				
2.2	36.5	10.1	22.1	<0.01	14.3	10.0	98.8	39.2		
2.0	32.3	9.0	26.4	<0.01	5.9	8.6	95.7	18.1		
1.8	30.3	8.4	24.4	<0.01	5.9	7.9	94.1	19.3		
1.6	27.8	7.8	24.9	<0.01	2.9	7.1	91.9	10.5		
1.4	23.4	6.5	21.3	<0.01	2.1	6.1	94.3	8.97		

The highest degree of iron removal was achieved at a high initial concentration of magnesium sulphate. Unfortunately, the high degree of iron removal is accompanied by quite substantial – almost 40% – wiping off magnesium. A high degree of iron removal, approximately 90%, was also obtained for lower initial concentrations of magnesium sulphate, accompanied by the decreasing magnesium loss. In the case of the crystallization of purified magnesium sulphate solution it is necessary to search for the optimum initial concentration of the solution being purified. This concentration cannot be too low because the solution must be concentrate and cannot be too high because the treatment is accompanied by quite a considerable loss of magnesium.

During the purification of magnesium sulphate solutions with the jarosite method it was shown that jarosite precipitated only with a relatively large excess compared to the stoichiometry of the precipitating reaction factor. Tables 4–6 show the results of the magnesium sulphate purification by the jarosite method by 400% (fourfold mass excess) with an excess of factor-losing stage, potassium jarosite (Table 4), sodium jarosite (Table 5) and ammonium jarosite (Table 6). Mass balances relate to 1.00 dm³ of purified magnesium sulphate solution. Precipitation was carried out at reflux in acidic solution (pH 1.2–2.0).

Table 4

Mass balance of the purification process by jarosite method (potassium jarosite)

$MgSO_4$ initial con- centration [mol/dm ³]	Concentration of magnesium and iron ion [g, mg]						Degree of Fe removal [%]	Loss of Mg [%]		
	before purification		after purification							
	solution		solution		precipitate					
	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]				
2.2	36.4	10.1	36.0	2.1	<0.01	7.9	78.6	1.13		
2.0	32.3	9.0	32.0	1.9	<0.01	7.1	78.6	0.99		
1.8	30.3	8.4	30.0	1.8	<0.01	6.5	77.6	0.96		
1.6	27.9	7.8	32.7	1.6	<0.01	6.1	78.8	4.20		
1.4	23.4	6.5	23.1	1.4	<0.01	5.0	77.9	1.37		

Table 5

Mass balance of the purification process by jarosite method (sodium jarosite)

$MgSO_4$ initial con- centration [mol/dm ³]	Concentration of magnesium and iron ion [g, mg]						Degree of Fe removal [%]	Loss of Mg [%]		
	before purification		after purification							
	solution		solution		precipitate					
	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]				
2.2	36.5	10.1	36.4	4.3	<0.01	5.7	56.6	0.30		
2.0	32.2	9.0	32.1	3.9	<0.01	5.1	56.1	0.37		
1.8	30.3	8.4	30.0	3.5	<0.01	4.7	56.2	0.83		
1.6	27.7	7.8	27.5	3.4	<0.01	4.3	55.9	0.72		
1.4	23.4	6.5	23.2	2.8	<0.01	3.7	56.4	1.11		

Table 6

Mass balance of the purification process by jarosite method (ammonium jarosite)

$MgSO_4$ initial con- centration [mol/dm ³]	Concentration of magnesium and iron ion [g, mg]						Degree of Fe removal [%]	Loss of Mg [%]		
	before purification		after purification							
	solution		solution		precipitate					
	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]				
2.2	36.5	10.1	36.3	2.4	<0.01	7.7	76.2	0.74		
2.0	32.3	9.4	32.1	2.2	<0.01	7.2	76.4	0.50		
1.8	30.3	8.4	30.0	1.9	<0.01	6.5	76.8	1.02		
1.6	27.7	7.7	27.5	1.8	<0.01	5.9	75.9	0.69		
1.4	23.4	6.3	23.2	1.4	<0.01	4.8	76.2	0.81		

In the case of potassium and ammonium jarosite high levels of iron removal from the solution of magnesium sulphate were reached. Table 7 shows the mass balance for 1000% (tenfold) stoichiometric excess of potassium sulphate, as obtained with the highest degree of conversion.

Table 7

Mass balance of the purification process by jarosite method (potassium jarosite)

$MgSO_4$ initial con- centration [mol/dm ³]	Concentration of magnesium and iron ion [g, mg]						Degree of Fe removal [%]	Loss of Mg [%]		
	before purification		after purification							
	solution		solution		precipitate					
	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]	Mg^{2+} [g]	$Fe^{2+/3+}$ [mg]				
2.2	36.4	10.1	36.3	<0.01	<0.01	9.8	96.8	0.19		
2.0	32.3	9.0	32.1	<0.01	<0.01	8.7	96.9	0.65		
1.8	30.3	8.4	30.2	<0.01	<0.01	8.2	97.0	0.30		
1.6	27.9	7.8	27.7	<0.01	<0.01	7.6	97.2	0.54		
1.4	23.4	6.5	23.3	<0.01	<0.01	6.3	97.1	0.55		

The loss of magnesium shown in table 6, regardless of concentration, does not exceed 1% of the magnesium content before treatment, with a high degree of iron removal. Unfortunately, the solution after the separation of potassium jarosite will contain a fairly significant amount of unreacted potassium sulphate, which will be crystallized together with magnesium sulphate heptahydrate. With continued land development it is not beneficial and troublesome.

4. Conclusions

This paper compares two methods for the purification of industrial magnesium sulphate solutions. In the case of the precipitation method a solution is obtained with a high degree of iron removal – about 99%, which is, however, accompanied by quite a considerable loss of magnesium sulphate. Magnesium sulphate passes to the precipitate in the form of magnesium hydroxide. In the case of the jarosite method using potassium sulphate as a precipitating factor, high degrees of iron removal were also obtained with a practically negligible loss of magnesium sulphate. Unfortunately, due to the further development of the purified magnesium sulphate in the presence of sulphates of ammonium, potassium or sodium, it is undesirable and problematic as it requires additional crystallization to remove the salt. Both methods of treatment, depending on conditions, provide a satisfactory degree of iron removal, however, the presence of other compounds than magnesium sulphate may limit its use after treatment, for example, the preparation of magnesium hydroxide of high purity.

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