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Acid Decomposition of Difficultly Soluble Potassium Ores with the Use of Organic Solvents

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Abstract—The dissolution of polyhalite ore in a hydrochloric acid solution at temperatures 50–100°C and salting out of potassium and magnesium sulfates from the obtained solutions with the use of selective organic solvents was studied. The effect exerted by temperature and solvent type on the extraction process was determined. A principal scheme of the ore processing was suggested.

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Potassium ores containing large concentrations of difficultly soluble minerals, such as langbeinite ($K_2SO_4 \cdot 2MgSO_4$), polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$), and kieserite ($MgSO_4 \cdot H_2O$), are low soluble in water and water-salt mixtures. Therefore, their processing with the use of mineral acids (HNO_3, H_3PO_4, HCl) is of considerable practical importance [1–3]. The methods and technologies developed to solve this problem allow intensification of the process and result in the production of complex fertilizers (NK-, NPK-, NKMg-, etc.) [1, 2, 4, 5]. At the same time, their industrial implementation is impeded by a number of circumstances. These are large energy consumption necessary for preparing products by the evaporation of final solutions and high cost of the reagents. Essential drawback of many technologies is conversion of sulfate ions constituting about 2/3 of the mass of the initial reagents to a large-tonnage gypsum residue upon the neutralization of acid salt solutions with lime. At the same time, potassium sulfate fertilizers are constantly in short supply at inner and world markets.

A possible way to solve this problem is acid processing of ores in the presence of organic solvents, which yields the possibility to selectively extract certain salts (sulfates or chlorides) from complex salt systems at a comparatively low cost and energy consumption [3,6].

In this study, a resource- and energy-saving acid processing of polyhalite ore into chloride-free potassium-magnesium fertilizer in the presence of organic solvent was developed. The conditions, at which separation of potassium and magnesium from ore into the solution is maximal, were found, an organic reagent was chosen, the conditions of the salting out potassium and magnesium sulfates from the obtained solution were determined, and a principal ore processing scheme was developed. The ore was dissolved in a solution of hydrochloric acid, which has high activity and low cost. It was suggested that the final product containing no more than 3% Cl may be obtained in the presence of an organic solvent. As salting out agents were tested five organic substances used in manufacture of mineral salts and fertilizers (acetone, methanol, ethanol, isopropanol, and isoamyl alcohol).

EXPERIMENTAL

The ore used in the tests was ground to 1-mm fraction and contained, on the average (wt %): K^+ 11.66, Mg^{2+} 3.25, Ca^{2+} 13.98, Na^+ 1.43, Cl^- 1.83, SO_4^{2-} 61.11, insoluble residue 0.90, and H_2O 5.90. The ore was dissolved in a thermostated reactor equipped with a stirrer in a hydrochloric acid solution under the following conditions: liquid-to-solid ratio l : s = 2 : 1, acid concentration 10 wt%, dissolution time 1 h, and temperature 50–100°C. After the test was complete, the suspension was separated by filtration under vacuum, the residue was washed with hot water onto a filter and

Table 1. Effect of temperature on ore dissolution

T, °C	Solution composition, wt %								Dissolution degree, %		
	K^+	Mg^{2+}	Ca^{2+}	Na^+	Cl^-	SO_4^{2-}	HCl	H_2O	K^+	Mg^{2+}	SO_4^{2-}
50	3.04	0.91	0.28	0.51	0.89	7.86	8.27	78.24	61.6	67.0	30.4
70	3.43	0.99	0.48	0.52	1.02	8.98	8.35	76.23	69.9	74.4	35.2
90	3.95	1.30	0.34	0.56	1.27	10.26	7.78	74.54	85.3	91.8	40.7
100	4.54	1.50	0.20	0.39	1.00	11.45	7.80	73.12	94.0	94.2	45.6

Table 2. Results of salting out of potassium and magnesium sulfates from a model solution

Organic reagent	Solution : reagent ratio	Concentration in salt precipitate, wt %			Salt yield, %;		
		K^+	Mg^{2+}	Cl^-	g/100 g solution	by K^+, %	by Mg^{2+}, %
Isopropanol	1:1	17.04	6.19	0.88	18.1	76.2	63.6
	1:1.5	16.42	5.93	0.86	20.3	82.4	68.2
	1:2	17.10	5.71	0.60	22.3	94.3	72.2
Acetone	1:1	18.16	5.70	0.63	12.1	54.5	39.2
	1:1.5	18.99	5.94	0.26	15.8	74.0	53.4
Methanol	1:1.5	36.31	1.17	0.81	9.4	84.7	6.3
	1:1	19.73	4.89	0.64	12.4	60.4	34.1
	1:1.5	21.42	5.05	0.71	17.2	90.8	49.4
	1:2	19.72	4.81	0.60	16.0	78.0	43.8
Isoamyl alcohol	1:1.5	0.05	9.34	–	1.2	–	6.3

repulped, and the forming gypsum was separated by decantation and filtered. The solid and liquid phases were analyzed in the course of tests. The data of the analysis were used to calculate the degree of dissolution of the ore components. Also, we studied a possibility of increasing the purity of the obtained gypsum by recrystallization.

Then, the ability of organic solvents to salt out potassium and magnesium sulfates from the acid salt solutions was studied. We used in the tests, first, a model solution, which was prepared by dissolving individual salts in a 10% HCl and contained (wt %): K^+ 3.69, Mg^{2+} 0.89, Cl^- 8.59 and then, the acid salt solution prepared by decomposing an ore of the composition (wt %): K^+ 4.55, Mg^{2+} 1.49, Ca^{2+} 0.15, Na^+ 0.70, Cl^- 8.18, SO_4^{2-} 11.68, H_2O, and the remainder 72.63. To the above solutions, a prescribed amount of organic solvent was added at 20°C and mixed for 40 min. Then, the suspension was filtered and weighed, and the solid and liquid phases were analyzed. The salt yield was determined by three procedures: 1) in grams of wet residue per 100 g of the acid salt solution; 2) by K^+, i.e., by the ratio of potassium mass in the precipitate to that in the initial solution (%); 3) by Mg^{2+}, i.e., by the ratio of magnesium mass in the precipitate to that in the initial solution.

According to the results obtained (Table 1), the extraction of potassium and magnesium sulfates into the solution in the course of the acid decomposition of the ore at 100°C is maximal. Under these conditions, polyhalite dissolved without the secondary crystal formation, which shows that the dissolution degree for potassium and magnesium is the same. The solution formed under these conditions is most saturated with useful components and the washed gypsum residue containing (wt %): K^+ 0.44, Mg^{2+} 0.26, Ca^{2+} 18.23, SO_4^{2-} 45.89, and H_2O 35.18 can be removed from the process without preliminary purification. In the temperature range 50–90°C the obtained solutions are less concentrated, with the dissolution degree of potassium lesser than for magnesium. The latter is due to crystallization of syngenite of the composition $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ [7]. Thus, for the acid decomposition of the ore at temperature of about 100°C is optimal. The dissolution degree of the useful components of the ore and, correspondingly, the purity of the final gypsum can be increased by additional recrystallization and washing

Table 3. Results of the experiments on salting out of potassium and magnesium sulfates from the acid salt solution

Organic reagent	Solution : reagent ratio	Composition of salt precipitate, wt %							Salt yield		
		K^+	Mg^{2+}	Ca^{2+}	Na^+	Cl^-	SO_4^{2-}	H_2O[a]	g/100 g solution	by K^+, %	by Mg^{2+}, %
Ethanol	1:1.5	18.91	2.18	4.40	0.66	45.51	0.63	27.71	20.7	86.2	61.1
	1:2	17.71	1.09	4.82	0.60	43.69	0.45	31.64	22.5	87.5	72.5
	1:3	19.55	0.80	4.84	0.39	45.06	0.50	28.86	21.7	93.2	70.5
Acetone	1:1.5	18.02	0.85	5.20	0.84	45.44	1.76	27.89	18.2	72.1	63.8
	1:2	20.28	1.16	5.00	0.61	46.33	1.20	25.42	18.6	83.1	62.4
	1:3	20.19	0.65	5.20	0.38	43.81	2.81	26.96	20.1	89.0	69.8
Methanol	1:3	31.40	0.18	0.31	0.92	42.03	0.27	24.89	12.9	89.0	2.7

[a] Total content of water and remaining components.

of insoluble residue. Recrystallization and drying of the precipitates obtained after the ore dissolution at 90 and 100°C yielded products containing 98–99% potassium sulfate semi-hydrate.

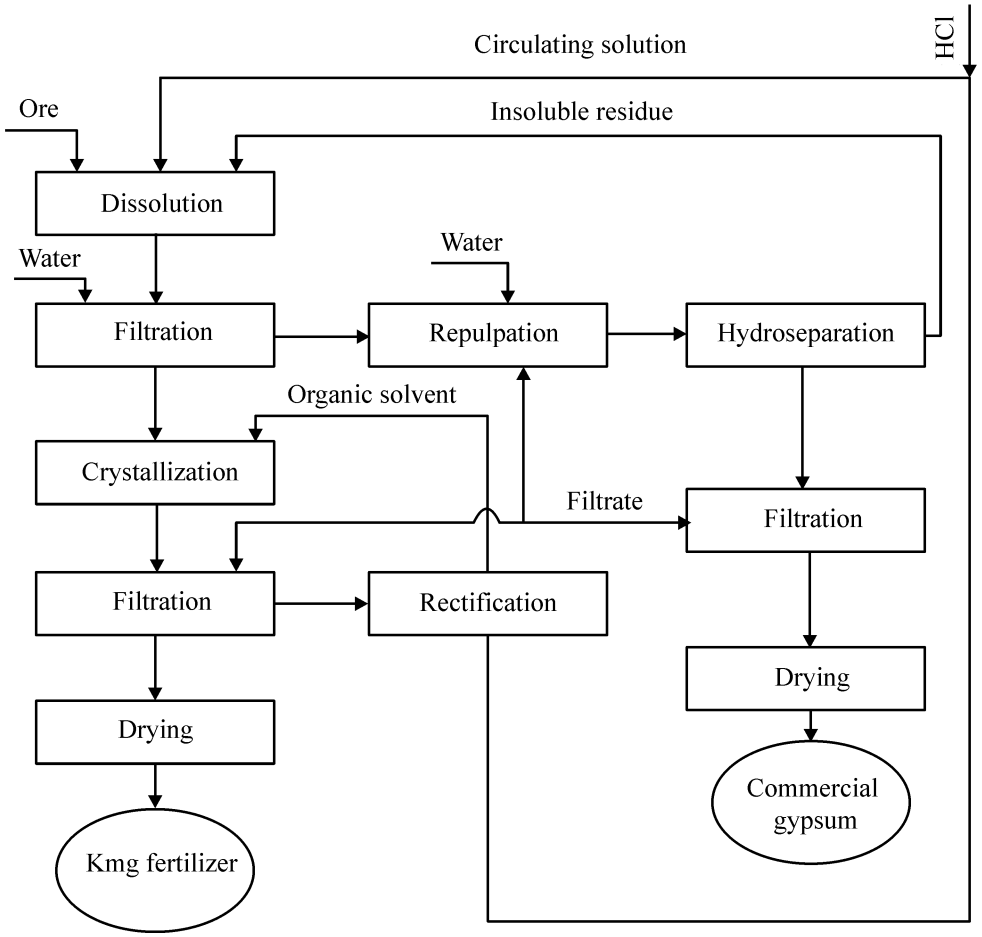
Study of the salting out of potassium and magnesium sulfates from a model acid salt solution in the presence of organic reagents showed that the extraction of the above salts in isopropanol and ethanol is maximal among the reagents studied (Table 2). For example, at the mass ratio between the solution and the reagent 1:1.5 the salt yield by K^+ was 81–82% for isopropanol and, 90% for ethanol whereas the salt yield by Mg^{2+} for ethanol was lower than for isopropanol (49% against 58–68%). This is because the amount of schoenite and potassium sulfate crystallizing in both solvents is different. In acetone, the yield by K^+ at the same solution : reagent ratio was somewhat lesser (74%) than in ethanol, whereas the yield by Mg^{2+} was larger by 4%. Unlike the above solvents, methanol, a strong salting out agent for potassium sulfate, salts out magnesium sulfate only slightly: the salt yield by K^+ was 85% and that by Mg^{2+}, only 6%. The least yield (only 6% for $MgSO_4$) was obtained in isoamyl alcohol, which cannot salt out K_2SO_4. All the solvents tested did not salt out chlorides. The residual content of Cl^- in the crystallized deposits (less than 1%) was caused by presence of an impregnating solution.

Increasing the content of the organic salting out reagent substantially increases the salt yield. For example, at the solution : reagent ratio = 1 : 1 a satisfactory yield of the salts was attained only in isopropanol, and at the ratio 1 : 1.5, in ethanol and acetone. Consequently, for the above solvents the latter ratio is optimal.

The results obtained show that isopropanol, ethanol, and acetone may be used for separation of potassium and magnesium sulfates from the acid salt solution. The use of isopropanol enters however a problem consisting in necessity of the development of a cyclic process. This must be done because isopropanol being evaporated forms an azeotropic mixture with water (88% isopropanol and 12% water), which would impede its regeneration in a pure form. For ethanol, formation of an azeotrope containing 4% water may be considered acceptable in this technology. Methanol can be used solely for separating potassium sulfate. Based on these results, ethanol, acetone, and methanol were used in the further study as salting out agents.

Results obtained in studying the salting out from a model solution were checked with acid-salt solutions prepared by dissolution of a polyhalite ore in a 10% hydrochloric acid. Most of them were confirmed (Table 3). Because the real solutions are more concentrated with the salts, the yield of potassium and magnesium sulfates from them was considerably higher. The highest salt yield was in ethanol, (20?22.5 g/100 g solution at the reagent : solution ratio = 1:(1.5–2). The yield in acetone was 18–19 g/100 g solution. In both solvents the salt yield by Mg^{2+} increased considerably (by 10–29%) and the yield by K^+ changed to a lesser extent. When the above ratio was increased further to 1:3, the salt yield in ethanol remained the same, whereas that in acetone increased by 8%. Consequently, the ratio 1:(1.5–2) is optimal. Noteworthy, the content of chlorides in the precipitates crystallized in acetone increased several-fold in comparison with precipitates obtained from a model solution, but this content did not exceed 3%. As in the previous experiments, potassium sulfate containing impurities of potassium and magnesium sulfates was crystallized in methanol. Drying of the salt precipitates in ethanol and acetone at optimal solution : reagent ratios

Principal scheme of ore decomposition



may yield a ballastless fertilizer containing (wt% in terms of dry product): K_2O 30–32, MgO 10–12, and Cl^- 1.2

For ore decomposition in the cycling mode, the most suitable reagents seem ethanol and acetone. Ethanol is cheaper than acetone. Also, it is less toxic, more explosion- and fire-proof, and more efficient. Acetone, however, needs considerably lesser energy expenditure for regeneration. Methanol can be recommended for technologies, in which a part of the product must be obtained in the form of potassium sulfate.

Based on the performed study, a new waste-free method was suggested for processing of polyhalite ore on potassium-magnesium sulfate fertilizer and commercial gypsum [6]. The principal scheme of the process involves dissolution of a polyhalite ore, preliminarily washed out of halite, in a circulating HCl solution at 100°C, filtering of the obtained suspension, washing of insoluble residue containing ore and gypsum with water onto a filter, dilution with water and solution, and following repulpation and hydroseparation of the suspension. Insoluble residue of ore is dissolved again. Finely dispersed gypsum is dried to obtain commercial product. After the insoluble residue is separated, the production solution is cooled down to 20°C and a circulating organic solvent is added to it to salt out potassium and magnesium sulfates. The salt precipitate being formed is settled, filtered, and washed onto a filter. KMg fertilizer is obtained from washed precipitate after drying. After separating sulfate salts, clarified mother liquor is used for rectification or distillation, and an organic solvent is recovered from it and used again for salting out. The remaining hot solution is used for ore dissolution. The losses are compensated by addition of fresh portions of the acid. Excess water may be removed from the process at the rectification stage to increase its amount in washing of salt precipitate and gypsum.

The process suggested here ensures virtually complete decomposition of the initial ore on a waste-less potassium magnesium sulfate fertilizer containing (wt %): K_2O

30–32, MgO 10–12, and Cl^- 1–2 and a 98–99% pure commercial gypsum, which can be used in construction material industry. The process uses constantly circulating reagents (organic solvent and hydrochloric acid), whose loss is inconsiderable. In this case, the energy expenditure for the regeneration of ethanol or acetone is lesser than for the evaporation of mother liquor by the known procedures.

CONCLUSIONS

(1). It reasonable to perform decomposition of polyhalite ore in hydrochloric acid solutions at a temperature of about 100°C in order to attain the maximum extraction of potassium and magnesium and avoid secondary crystal formation.

(2) The recrystallization and washing of insoluble residues after ore dissolution ensures increase to 97% of the dissolution degree of potassium and magnesium and yields, after drying, commercial gypsum, in which content of potassium sulfate semi-hydrate is 98–99%.

(3) The salting out of potassium and magnesium from the acid salt solutions in isopropanol and ethanol is maximal and that in acetone is somewhat lesser. The mass ratio between the solution and the reagent 1:(1.5–2) is optimal. In methanol, potassium sulfate salts out together with impurities of calcium and magnesium sulfates.

(4) For cycling ore decomposition, the most suitable organic reagents are ethanol and acetone.

(5) The new technology of the decomposition of polyhalite ore in the presence of an organic reagent allows chloride-free potassium-magnesium fertilizer and commercial gypsum to be obtained at low consumption of the reagents and low energy expenditure, compared with the known methods.

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