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Original Article

Flotation of sylvinite from Thakhek, Lao, P.D.R.

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Abstract

The purpose of this research is to study about sylvinite flotation. Both chemical and operating variables are main factors in this cationic flotation study. The chemical factors consist of mineralogy, solubility, amine dosages and types of frothers: pine oil and MIBC added. The operating factors, controlling flotation kinetics, compose of particle size, agitation intensity and conditioning time. Mineral characterization was carried out using XRD technique. From the XRD trace, both sylvite (KCl) and halite (NaCl) are major minerals. Therefore, a sampled potash ore from Thakhek, Lao, P.D.R. can be characterized as sylvinite. And ore solubility is 84.2 g/100 g water at 34°C. Chemical analysis of this ore was conducted using AAS technique. It is coincide with the mineralogical analysis that KCl and NaCl are the major components with some minor $KCl·MgCl_2·H_2O$. Both grade and recovery of the rougher concentrates were used to measure the flotation efficacy. Chemically, an optimum flotation of sylvinite in the saturated brine with amine and MIBC was found at the dosages of 150 and 50 g/ton ore respectively, yielding 41.5% K_2O with 95.9% recovery. Operationally, an optimum flotation of 30-mesh sylvinite with the indicated amine and MIBC dosages at the agitation intensity of 1000 r.p.m and 9-minute conditioning time yields 39.1% K_2O with 94.2% recovery. Furthermore, the flotation kinetics follows the first-order rate law with rate constant of 1.41 sec^{-1}. Suggested that direct cleaner and/or re-cleaner flotation with reagent combinations of both collector and frother, or reverse flotation of the retaining halite using alkyl morpholine as a collector could enhance the final concentrate grade up to 60% K_2O complying with the fertilizer industry.

Keywords: cationic flotation, chemical and operating factors, potash, sylvinite

1. Introduction

Potassium (K) is one of the vital elements for plants. It encourages plants to uptake water, to make better use of light and air, and to increase diseases resistance. Above all it is necessary for the development of flowers and fruits (Anon, 2016). Most of the potassium element derives from potash minerals such as sylvite (KCl), sylvinite (KCl·NaCl) carnallite ($KCl·MgCl_2·H_2O$), etc. Each mineral contains potassium oxide (K_2O) in a certain amount. However, the specification of fertilizer grade mineral is about 60% K_2O. As surveyed by Department of Primary Industries and Mines (2014), the ASEAN country and Thailand consume potash about 3 and 0.7 million tons per year in respect. Nonetheless, only tiny amount of production comes from Laos even there are huge potash reserves in the northeast Thailand and Lao, P.D.R. border. Therefore, the Joint R&D on ASEAN fertilizer minerals has been proposed by Rattanakawin (2014) because potash is one of the crucial sources of fertilizers in this agricultural region.

Potash was first processed in the 19th century by hot leaching and crystallization of potassium salts from saturated saline solution (Titkov, 2004). However, this process consumes high heat energy (95-100°C) and causes high corrosion of the process equipment. Thus flotation of potash in saturated brine solution has been implemented instead. At present, over 75% of the potash production worldwide comes from cationic flotation with amine as collector. Especially, the flotation of sylvite by using primary aliphatic amine with hydrocarbon chain length of C_{16}-C_{18} is practically done. Contrary to sylvite, sylvinite and/or carnallite are not subject

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to float successfully in terms of grade and recovery. Therefore, the purpose of this research is to study effects of chemical and operating factors on sylvinite flotation. The chemical factors consist of mineralogy, solubility, amine dosages and types of frothers (pine oil, and methyl isobutyl carbinol: MIBC) added. And the operating factors controlling flotation kinetics compose of particle size, agitation intensity and conditioning time. Ultimately, the final concentrate grade should achieve 60% K_2O complying with the fertilizer industry.

2. Methods

2.1 Characterization

A potash ore was sampled from Sino-Agri Potash Mine, Thakhek, Lao, P.D.R. The sample was characterized for its mineralogical and chemical composition, and solubility. The mineralogical study was done by X-ray diffraction (XRD) using D8-Advance BRUKER linked with Intel Pentium IV Processor. The measuring conditions were as follows: Cu K-alpha (λ = 0.15406 nm) radiation at 40 KV and 40 mA; start and stop angles at 5 and 78 degrees; scanning speed of 0.2 sec/step with increment of 0.02; detection with scintillation counter. The -200 mesh sample was packed into a hole on plastic plate. After that the well-packed sample was x-rayed with the above-mentioned conditions. The intensity of detected signals was then plotted as a function of 2θ. Finally the intensity peaks were selected, searched and matched with those of the standard minerals compiled by the JCPDS using computer program DIFFRAC PLUS.

The chemical composition of samples from flotation products (feed, concentrate and tailing) was analyzed using Perkin Elmer, Model 3310 atomic absorption spectrometer (AAS) at the wavelength of 589.0, 766.5 and 285.2 nm for sodium (Na), potassium (K) and magnesium (Mg) elements in respect. Solubilities of the analytical grades sodium chloride (NaCl), potassium chloride (KCl) and magnesium chloride ($MgCl_2$), and that of potash ore were studied in order to obtain data about points of those saturated brine. All salts were slowly dissolved in 100 ml water and agitated with magnetic stirrer up until reaching theirs saturation points. After that the solubilities of those salts were determined using gravimetric method.

2.2 Flotation

Processing of a potash ore was conducted by means of froth flotation. Cationic flotation of that run-of-mine (ROM) ore was performed in the saturated brine. In short, the procedure of batch flotation using Denver machine (Denver D-1, Serial no. 95671-1) was as followed:

1. Mill 4000 g of the ROM ore using granite mortar and pestle, and screen the milled product to different sizes of 14, 18, 30 and 60 U.S. mesh corresponding to 1.4, 1.0, 0.60 and 0.25 mm respectively.
2. Prepare 250 ml saturated brine by dissolving the fine ROM ore in water.
3. Add 250 g of the milled product in the well-prepared brine.
4. Condition the saturated pulp in the flotation cell at 750, 1000 or 1250 r.p.m. with the collector (amine) at various concentrations (100, 150, 200 or 250 g/ton ore) for 3, 6, 9 or 12 min.
5. Add the frother (pine oil or MIBC) about 50 g/ton ore.
6. Float KCl as a concentrate for 3 min.
7. Discard sink product, mostly NaCl, as a tailing.
8. Filter, dry, weigh and analyze the assays of feed, float and sink products by using AAS.
9. Examine mineralogical characteristic of the selected concentrate using XRD.
10. For the flotation kinetics experiment, collect the froth for cumulative times of 15, 30, 45, 60, 90, 120 and 360 sec in different pans. All products were filtrated, dried, weighed and assayed by AAS.
11. Evaluate the flotation performance by using grade (%K_2O) and recovery (%R) as parameters. Calculate the %R using the 3-product formula on the basis of product grades as: % = R[f) – (t c] / [c) – (t f] * 100where f, c and t are assays of feed, concentrate and tailing respectively.

More information regarding experimental procedures of soluble salts flotation and flotation rate has been described by Rattanakawin (2015) at length.

3. Results and Discussion

3.1 Mineralogical composition

The sharp XRD trace of a potash ore (Figure 1) shows clearly that sylvite (KCl) and halite (NaCl) are major constituents. Sylvite displays the main peaks at 2θ = 28.4, 40.6, 50.3 and 58.8 degrees of planes (200), (220), (222) and (400), respectively (JCPDS No. 01-073-0380). Besides, the peaks of halite at 2θ = 31.7, 45.4 and 56.2 degrees of planes (200), (220) and (222) are also illustrated (JCPDS No. 00-05-0628). As a result, this ore (mixture of sylvite and halite) is characterized as sylvinite.

3.2 Chemical composition

Chemical composition of a potash ore is as follows: 32.2%KCl, 61.2% NaCl, 0.51% $KCl{\cdot}MgCl_2{\cdot}H_2O$ and 6.09% others. It is coincide with the mineralogical composition that sylvite and halite are major components with some minor carnallite. Indeed, this potash ore is sylvinite. It should be noted that all components are categorized as soluble salt minerals in the context of flotation chemistry (Fuerstenau, Miller, & Kuhn, 1985). Then this soluble salt (sylvinite) must float only in the proper saturated brine.

3.3 Solubility

Solubilities of NaCl, KCl, $MgCl_2$ and a potash ore at 34°C are 37.5, 35.2, 342 and 84.2 g/100g water respectively. To prepare the proper saturated brine for sylvinite flotation, a potash ore was chosen because its solubility is greater than those of NaCl and KCl. The $MgCl_2$ was not selected because it has very high solubility. It also has less content in a potash ore studied. Moreover this alkaline earth salt is usually discarded as bittern. With a small amount of this salt content in any saline solution, it will deteriorate performance of a KCl flotation (Weedon, Grano, Akroyd, Goncalves, & Moura, 2007).

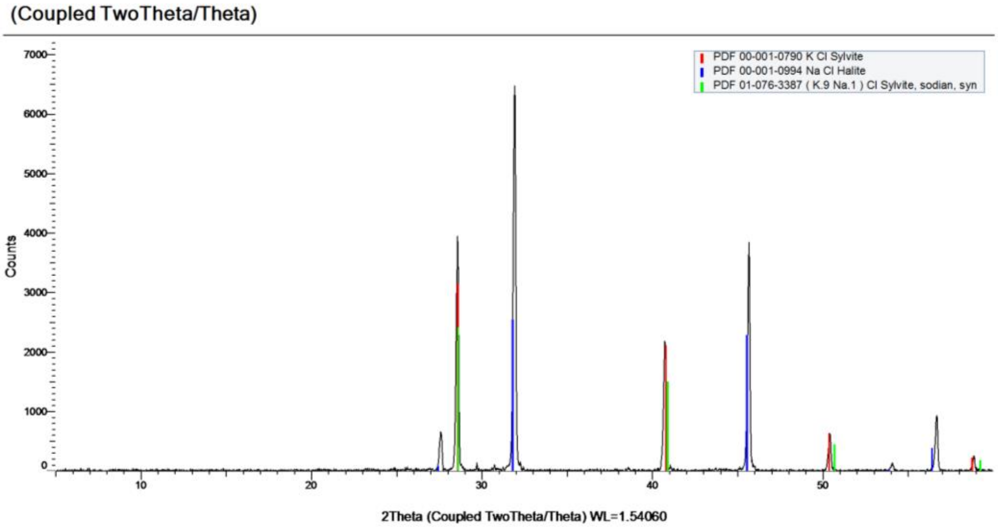

Figure 1. XRD trace of a potash ore.

3.4 Effects of chemical factors on sylvinite flotation

Effects of chemical factors on cationic flotation of sylvinite were studied as a function of amine dosages with different frothers: pine oil and MIBC. The results of amine flotation with pine oil and MIBC were presented in Table 1 and 2 respectively. It was found that amine dosages which greater than 150 g/ton ore yield average recovery of 90.6% (pine oil) and 94.9% (MIBC) with both concentrate grades averaging ~ 40% K_2O. On the other hand, the average grades of tailings are 1.46% and 0.77% K_2O with pine oil and MIBC in respect. It is appearance from Figure 2 that MIBC (b), comparing to pine oil (a), is the suitable frother in terms of grade and recovery for this amine flotation. The flotation result is in accordance with that of Laskowski, Wang, and Alonso (1996) who indicated that MIBC improves colloidal dissolution of amine in brine. Also, the results are always better when MIBC and amine are mixed and added together to the flotation system.

The optimum dosages of amine and MIBC for sylvinite flotation are 150 and 50 g/ton correspondingly. This optimum condition yields 95.9% recovery with concentrate grade of 41.5% K_2O comparing to 38.7% K_2O with 96.6% recovery from 250 g/tom amine flotation. In order to verify chemical composition of this optimum concentrate, XRD semi-quantitative analysis was carried out and shown in Figure 3. The mineral composition and grade quite corresponds well with those from the chemical analysis. Nonetheless, the K_2O content in this rougher concentrate is lower than 60% which is not conform to the fertilizer market.

3.5 Effects of operating factors on sylvinite flotation

Effects of operating factors on flotation of sylvinite with amine and MIBC at the dosages of 150 and 50 g/ton ore respectively were studied as a function of particle size, agitation intensity and conditioning time. The effects of particle size on recovery and grades of the flotation at agitation intensity of 1000 r.p.m. with 3-minute conditioning

Table 1. Chemical analyses of flotation products and recovery of sylvinite as a function of amine dosages with 50 g/ton pine oil.

Amine dosage (g/ton ore)	Product	Grade (% K_2O)	% Recovery
100	Feed	8.42	69.9
	Concentrate	40.4	
	Tailing	2.96	
150	Feed	12.3	89.2
	Concentrate	38.2	
	Tailing	1.86	
200	Feed	11.7	90.8
	Concentrate	42.3	
	Tailing	1.44	
250	Feed	10.4	91.9
	Concentrate	41.2	
	Tailing	1.09	

Table 2. Chemical analyses of flotation products and recovery of sylvinite as a function of amine dosages with 50 g/ton MIBC.

Amine dosage (g/ton ore)	Product	Grade (% K_2O)	% Recovery
100	Feed	10.2	75.5
	Concentrate	36.8	
	Tailing	3.17	
150	Feed	9.11	95.9
	Concentrate	41.5	
	Tailing	0.47	
200	Feed	11.9	92.1
	Concentrate	39.0	
	Tailing	1.30	
250	Feed	11.5	96.6
	Concentrate	38.7	
	Tailing	0.54	

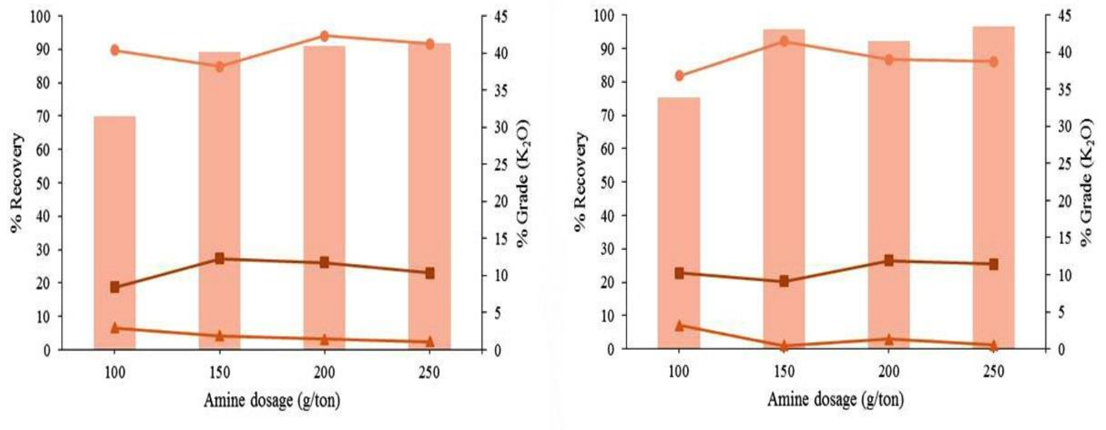

Figure 2. Flotation recovery and grades of sylvinite as a function of amine dosages and frother types; (a) pine oil and (b) MIBC.

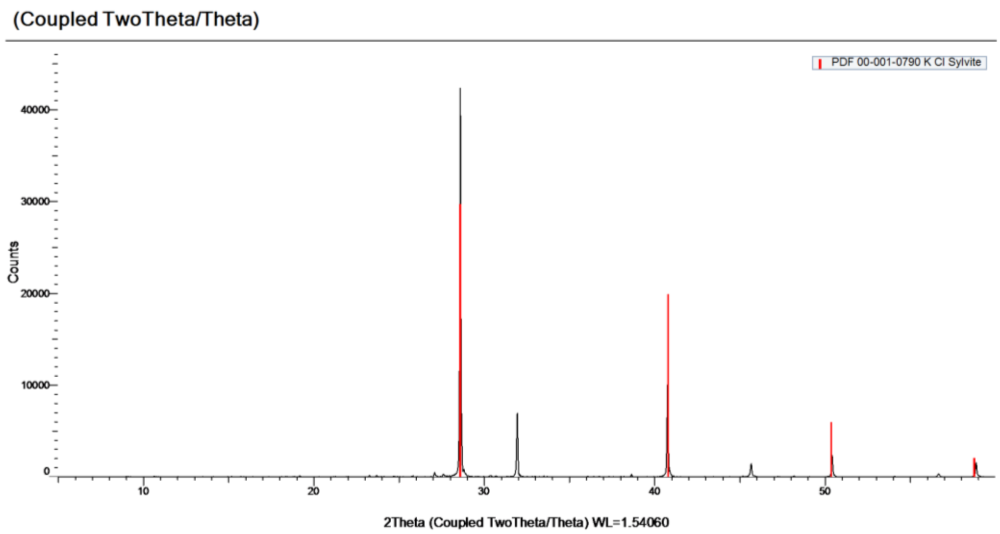

Figure 3. XRD trace of a concentrate from the optimum flotaton of sylvinite with 150 g/ton amine and 50 g/ton MIBC.

time are presented in Figure 4. It was found that 30-mesh (0.6 mm) sylvinite is suitable for this flotation yielding recovery of 95% with concentrate grade of 34.4% K_2O. Therefore, this 30-mesh size was used in the following studies on the effects of agitation intensity and conditioning time on the sylvinite flotation. It was used in the flotation kinetics experiment as well.

Effects of agitation intensity on recovery and grades of 30-mesh sylvinite with 3-minute conditioning time are shown in Figure 5. Found that the agitation intensity of 1000 r.p.m. gives the optimum flotation in terms of recovery and grade. Then this intensity value was used in further studies on the effects of condition time and rate on the flotation.

Effects of conditioning time on recovery and grades of 30-mesh sylvinite at the agitation intensity of 1000 r.p.m. are illustrated in Figure 6. Even though the 3-minute conditioning time gives a slightly higher recovery than that of the 9-minute one, but the latter conditioning time yields much higher grade than that of the former. Therefore, the 9-minute conditioning time was eventually used in finding the order and rate constant of the flotation kinetics.

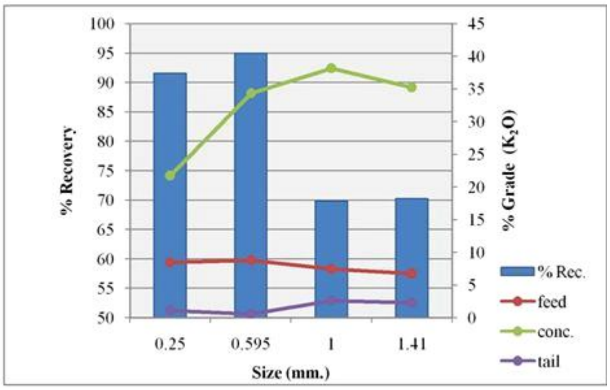

Figure 4. Effects of particle size on recovery and grades of sylvinite flotation at the agitation intensity of 1000 r.p.m. with 3-minute conditioning time.

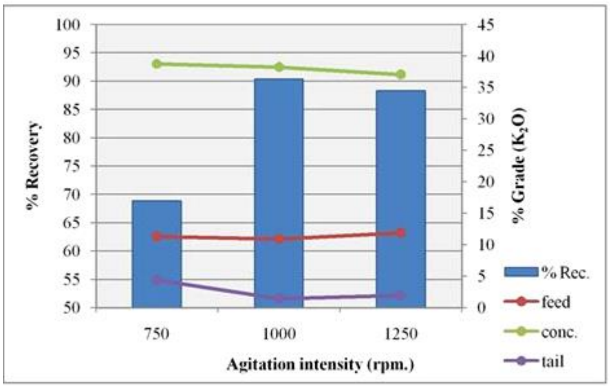

Figure 5. Effects of agitation intensity on recovery and grades of 30-mesh sylvinite flotation with 3-minute conditioning time.

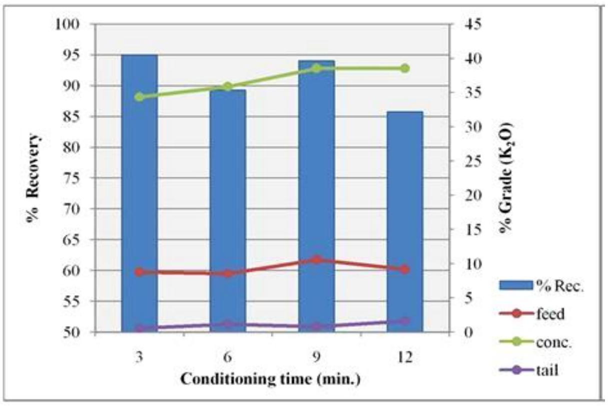

Figure 6. Effects of conditioning time on recovery and grades of 30-mesh sylvinite flotation at the agitation intensity of 1000 r.p.m.

A batch flotation of 30-mesh sylvinite at the agitation intensity of 1000 r.p.m with 9-min conditioning time was performed. Metallurgical balance and kinetics plot of this flotation are shown in Table 3 and Figure 7 respectively. It can be seen that the first order rate law is quite valid for this flotation with rate constant of 1.41 sec^{-1} yielding the optimum grade and recovery of 39.1% K_2O and 94.2% in respect. However, the K_2O content in this rougher concentrate is lower than 60% which is not conform to the fertilizer market. Therefore, the cleaner and/or re-cleaner stages are suggested to increase the content using both direct and reverse flotation. Direct flotation of sylvinite could be done using hydrogenated tallow alkylamine acetate or other tailor-made cationic collectors. On the other hand, alkyl morpholine or other custom-made anionic collectors could be used to do reverse flotation of halite retaining in the concentrate.

4. Conclusions

The ROM potash ore from Thakhek, Lao, P.D.R. can be characterized as sylvinite because sylvite (KCl) and halite (NaCl) are major minerals. This ore composes mainly of 32.2% KCl, 61.2% NaCl, and 0.51% $KCl.MgCl_2$. Ore solubility is 84.2 g/100 g water at 34^{o}C. Chemically, the optimum flotation in the saturated brine with amine and MIBC is found at the dosages of 150 and 50 g/ton ore respectively, yielding 41.5% K_2O with 95.9% recovery. Operationally, the optimum flotation of 30-mesh sylvinite with the indicated amine and MIBC dosages at the agitation intensity of 1000 r.p.m and 9-minute conditioning time yields 39.1% K_2O with 94.2% recovery. Furthermore, the flotation kinetics follows the first-order rate law with rate constant of 1.41 sec^{-1}. It is suggested that direct cleaner and/or re-cleaner flotation with reagent combinations of both collector and frother, or reverse flotation of the retaining halite using alkyl morpholine as a collector could enhance the final concentrate grade up to 60% K_2O complying with the fertilizer industry.

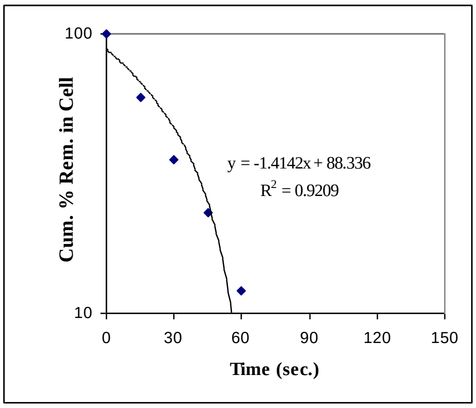

Figure 7. Cummulative % remaining in cell and time plot from a batch flotation of 30-mesh sylvinite at the agitation intensity of 1000 r.p.m with 9-minute conditioning time.

Table 3. Metallurgical balance of a batch flotation of 30-mesh sylvinite at the agitation intensity of 1000 r.p.m with 9-minute conditioning time.

Time (sec.)	% Wt.	% K2O	Units	% R	Cum. % R	Cum. % Rem
0	0.00	9.79	0.00	0.00	0.00	100.00
15	18.26	40.16	733.32	40.84	40.84	59.16
30	10.28	41.50	426.62	23.76	64.59	35.41
45	6.14	36.48	223.99	12.47	77.07	22.93
60	5.08	38.48	195.48	10.89	87.95	12.05
90	3.57	30.12	107.53	5.99	93.94	6.06
120	2.56	12.21	31.26	1.74	95.68	4.32
360	5.91	2.76	16.31	0.91	96.59	3.41
Residue	48.20	1.27	61.21	3.41	100.00	0.00
Total	100.00	17.96	1795.72			

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