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Production of glaserite and potassium sulphate from gypsum and sylvinite catalysed by ammonia

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Abstract

Ammonia has the property of markedly depressing the solubilities of certain inorganic salts while hardly affecting the solubilities of others. Because of this property ammonia can be used to promote various crystallization processes and some double decomposition reactions between inorganic salts. This paper examines two examples of the second type of application in which gypsum produced from seawater salt plants and sylvinite $KCl \cdot NaCl$ are reacted in aqueous ammonia resulting in the formation and selective crystallization of glaserite, and secondly the glaserite formed is reacted with sylvinite to produce potassium sulphate. Experimental work is described which follows the progress of the reactions under a wide range of conditions. Some of the results give above 98% overall yield of high purity potassium sulphate. © 1997 Elsevier Science S.A.

Keywords: Glaserite; Potassium sulphate; Gypsum; Sylvinite

1. Introduction

Interest in potassium sulphate stems mainly from its use as a potash fertilizer for crops which are sensitive to chlorides. This fertilizer is usually manufactured by double decomposition of potassium chloride and one of the various salts which contain magnesium sulphate [1–3], such as kainite $KCl \cdot MgSO_4 \cdot 3H_2O$, langbeinite $K_2SO_4 \cdot 2MgSO_4$, leonite $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ and schonite $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. As the world's rich sources of magnesium sulphate become rapidly depleted, new raw materials must be found to supply the sulphate. Potassium chloride is relatively abundant; common sylvinite ores contain about 40–70% NaCl and 60–30% KCl, but expensive potassium chloride up-grading treatments of these ores are required to render the potassium chloride usable for the production of potassium sulphate. Therefore, new processes should be found which do not use the conventional materials. Gypsum and sylvinite are widely available in nature and as by-products from seawater solar salt plants.

A significant amount of work on the production of potassium from natural gypsum and potassium chloride has been reported [4–6]. The basic reaction describing the process is:

$$CaSO_4 \cdot 2H_2O + 2KCl \rightleftarrows K_2SO_4 \downarrow + CaCl_2 + 2H_2O \tag{1}$$

In aqueous systems containing no ammonia the Eq. (1) gives syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ and/or pentasalt $K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$. The double salts can be subsequently decomposed to K_2SO_4, but the overall yield of these processes is low.

Previous works have shown that high yields of K_2SO_4 can be obtained if Eq. (1) is conducted in aqueous ammonia [7–12], and in aqueous hydrazine [8,13]. These additives promote the formation of K_2SO_4 and prevent the systems from moving toward the syngenite field.

The research described here concerns the fabrication of glaserite and K_2SO_4 from gypsum produced from seawater bittern and sylvinite $KCl \cdot NaCl$ in aqueous ammonia systems under a wide range of operational conditions. The basic reactions describing the process are:

$$4CaSO_4 \cdot 2H_2O + 6KCl \cdot X NaCl \rightleftarrows 3K_2SO_4 \cdot Na_2SO_4 \downarrow + 4CaCl_2 + (X-2)NaCl + 8H_2O \tag{2}$$

followed by:

$$3K_2SO_4 \cdot Na_2SO_4 + 2KCl \cdot X NaCl \rightleftarrows 4K_2SO_4 \downarrow + (2+X)NaCl \tag{3}$$

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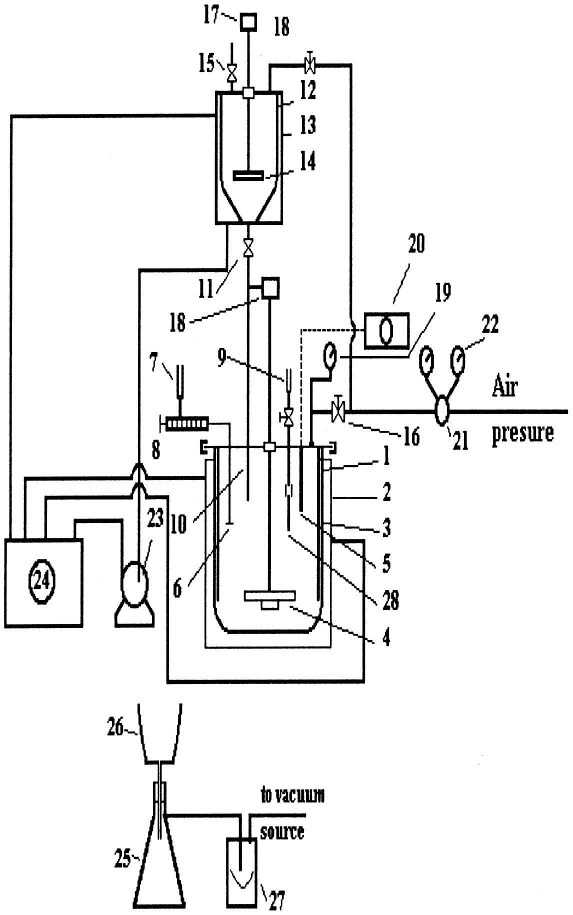

Fig. 1. Experimental set-up. (1) Reactor crystallizer vessel, (2) reactor crystallizer jacket, (3) baffles, (4) turbine impeller, (5) thermocouple probe, (6) solution sampling filter, (7) pipet sampling port, (8) micro-sampling valve, (9) reactor charge port and solids sampling port, (10) injector discharge port, (11) injector outlet valve, (12) injector, (13) injector jacket, (14) injector turbina impeller, (15) injector charge port, (16) pressurization ports, (17) injector stirrer motor, (18) reactor stirrer motor, (19) reactor pressure gauge, (20) temperature recorder, (21) pressure regulator, (22) pressure regulator gauges, (23) coolant pump, (24) constant temperature circulating systems, (25) filtration flask, (26) filtration funnel, (27) absorption flask and (28) solid sampling adapter.

2. Experimental

2.1. Apparatus

The principal equipment used in this work is presented in Fig. 1, the main item being the stirred batch reactor crystallizer. This was a cylindrical glass vessel, 100 mm internal diameter by 130 mm height, equipped with a four-blade propeller stirrer and two vertical, evenly-spaced baffles. Another important unit was the injector, it consisted of two concentric 80 mm and 120 mm internal diameter mild steel tubes, 150 mm long; this unit was used to inject aqueous ammonia solutions into the reactor crystallizer. The temperature in both units was kept constant by cooling water circulated through the jackets from a constant temperature circulating system. Clear samples of the liquid in the reactor were obtained via a 2 mm internal diameter tube installed through the reactor top cover.

2.2. Procedure

The constant temperature circulating bath was set to the desired temperature, with circulation through both reactor and injector vessel jackets. Sylvinite was weighed and charged into the reactor and a weighed amount of gypsum and 350 ml of aqueous ammonia were charged to the injector. The gypsum–solvent mixture was stirred until it reached a set temperature and then was discharged into the reactor. The stirrer speed in the reactor was adjusted to the desired value. The course of the reaction was followed by determining the amount of calcium ion in solution by titration with 0.01 M EDTA (1 ml of 0.01 M EDTA = 0.4008 mg Ca) using murexide indicator. To clear the sampling tube of liquid from prior aliquots, the first 1 ml sample was drawn into the 1 ml pipette and discarded.

2.3. Materials

The reactants used in this work included gypsum, produced as by-product from a local seawater solar salt plant, of purity 98.5 wt%, milled to pass through a 62 μm sieve aperture, potassium chloride and sodium chloride of purity 99.5%, both milled to pass through a 125 μm sieve aperture. Mixtures of KCl with NaCl were prepared to simulate the natural sylvinite.

2.4. Calculations

In the first stage of the process it is very important to achieve a high yield of the more valuable product, namely K_2SO_4 as glaserite, from the more expensive reactant, KCl. Therefore, the experimental results obtained have been presented in terms of potassium converted to glaserite as given by Eq. (4),

$$\%\ \text{yield} = \frac{\text{K equivalent to Ca content of 1 ml sample} \times V \times 100}{\text{Total K charged to the reactor}} \qquad (4)$$

However, to obtain the precise value of the yield it was necessary to accurately estimate the total volume, V, of the solution in the slurry at each sampling time so that the total amount of calcium reacted could be calculated [8].

For every sample taken, V, was calculated from the initial volume of aqueous ammonia charged to the reactor, with corrections made for the amount of water produced in the reaction, substraction of 2 ml of solution taken at each sampling, volume increase due to dissolved KCl and NaCl and volume change due to the conversion of KCl and NaCl to $CaCl_2$.

Three additional corrections were made for the dissolved ionic species removed in each sample aliquot, these species were K^+, Na^+ and Ca^{2+}. An iterative procedure was needed. Two iterations were sufficient to establish the conversion to within 0.1% accuracy.

2.5. *Proposed process*

In brief, the process consists of three major stages. In the first stage gypsum is reacted with sylvinite in aqueous ammonia to give glaserite as the intermediate product which is separated from the mother liquor by filtration. In the second stage glaserite is converted with sylvinite to K_2SO_4 in aqueous ammonia. In the third stage the ammonia is recovered from the filtrates of the first stage by distillation and recycled to the process. The filtrates and washings from the second stage filter may be recycled to the first stage.

In a continuous process the recovery of ammonia from the glaserite reactor exit liquid by distillation should not present problems and losses should be low. In the past, plants using the Solvay process operated with many recirculating streams containing ammonia without significant losses.

3. Results and discussion

3.1. *Preliminary experiments on the influence of Eq. (2)*

A series of preliminary experiments were carried out to assess the influence on Eq. (2) of the following variables, the effects of which were then eliminated from later studies.

3.1.1. *Stirrer speed*

The rate of reaction and yield were found to be independent of the speed of agitation above 300 rpm. This appeared to be the minimum speed required to give a uniform suspension in the reactor. A speed of 400 rpm was chosen for all further runs.

3.1.2. *Gypsum grain size*

Trials with two batches of gypsum milled to pass through 62 μm and 100 μm sieve apertures were conducted. The results showed 4–5% higher rate of reaction and yield for the smaller grain size. Therefore, gypsum of finer grain size was used for all further tests.

3.1.3. *Ammonia concentration*

Trials with three different ammonia concentrations of 30, 35 and 40% (w/w) were conducted. The runs with the two higher concentrations showed similar high rates of reaction and high yields. the run with the lower ammonia concentration gave a final yield of only 55%; X-ray powder diffraction analysis of this solid showed high proportion of syngenite. The ammonia concentration of 36.5% (w/w) was chosen for all further tests in order to limit the operating pressure in the reactor to the region of 1 bar.

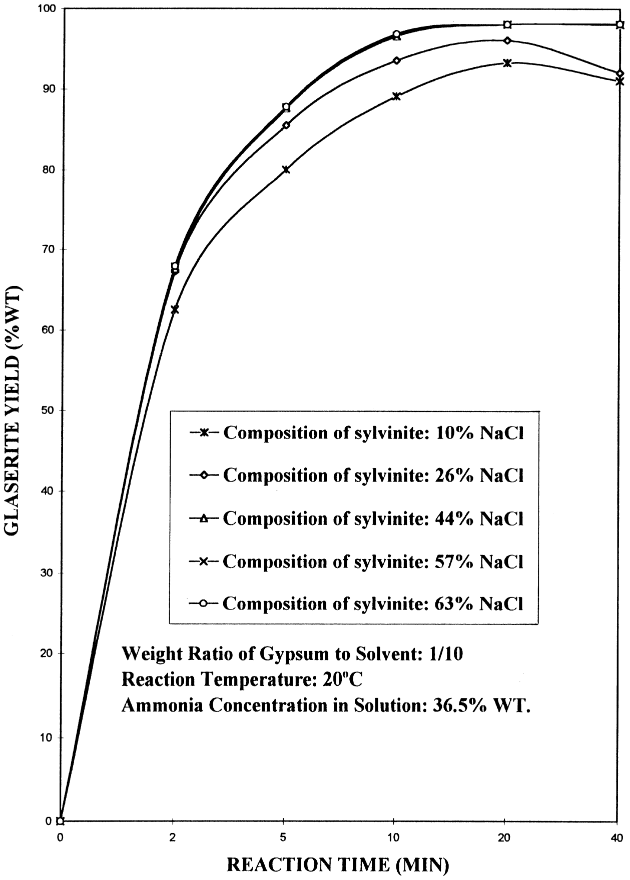

Fig. 2. Effects of different sylvinite compositions on gypsum conversion.

3.1.4. *Sylvinite grain size*

Trials with two batches of sylvinite having different particle size distributions showed no difference in the rate of reactions and yields. This was expected since sylvinite is the more soluble of the two reactants. The sylvinite used in further tests was milled to pass through a 125 μm sieve aperture.

3.2. *Important variables*

The following three variables were found to exert considerable influence on the course of Eq. (2): (i) composition of sylvinite, (ii) gypsum to solvent ratio and (iii) reaction temperature. Information on these variables is given here, together with information on glaserite composition and glaserite conversion to K_2SO_4.

3.2.1. *Variation of sylvinite composition*

Five runs were carried out to assess the effects on the reaction of changing the composition of the sylvinite. Other variables which might affect the reaction were maintained constant for these runs, these included initial gypsum to solvent ratio 1 : 10, gypsum to KCl ratio 2 : 3 and reaction temperature 20.0 °C. The results are shown in Fig. 2, in which the gypsum conversion to glaserite is plotted against time for each of the five runs. These curves show clearly that higher yields and higher rates of conversion are obtained with

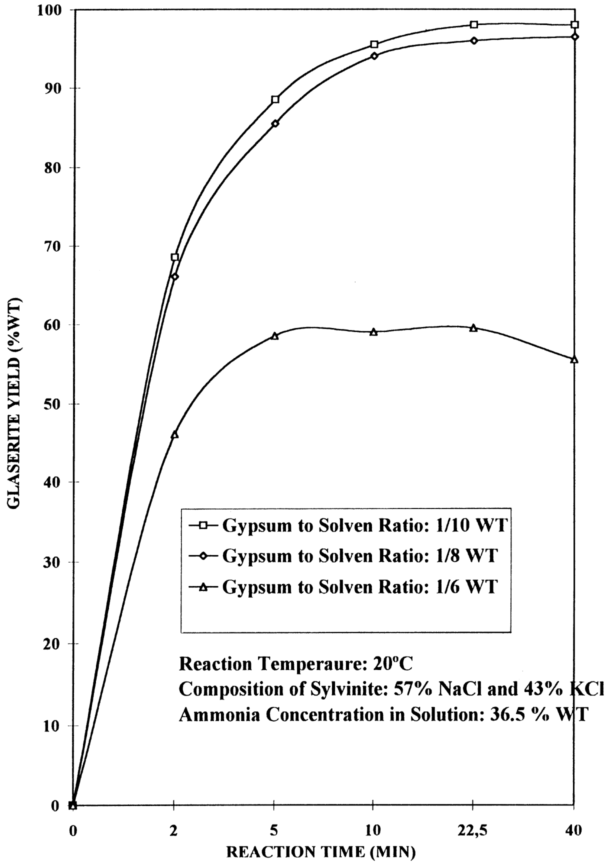

Fig. 3. Effects of different gypsum to solvent ratios on gypsum conversion.

sodium chloride rich sylvinite containing 44, 57 and 63% NaCl than with sylvinite containing 26% and 10% NaCl. An interesting feature of these curves is their tendency toward the same values of conversion at higher NaCl concentrations. All five curves show a rapid rate of conversion up to a residence time of about 5 min, then a gradual increase up to about 20 min, after which the three curves for higher NaCl concentrations level off. This levelling in the reaction rate prior to complete conversion is attributed to the formation of an impenetrable film of glaserite over the less reactive gypsum crystals. The other two curves for 10 and 26% NaCl show a significant decrease in yield for residence time above 20 min, attributed to the formation of syngenite. Apparently NaCl acts in two ways: (i) during the reaction it increases the rate of formation and yield of glaserite, and (ii) it changes the solubility relationships of the different salts present in the ammoniacal system, leading to the annulment of syngenite formation.

3.2.2. Variation of gypsum to solvent ratio

The effects on the reaction of changing the gypsum to solvent ratio were investigated by carrying out three runs with the following ratios: 1 : 10, 1 : 8 and 1 : 6 by weight. Other variables which affect the reaction were maintained constant for these runs; these included NaCl content in the sylvinite 57%, gypsum to KCl ratio 2 : 3 and reaction temperature 20 °C. These results are presented in Fig. 3, showing that for the ratios of 1 : 10 and 1 : 8 similar curves of conversion against time are followed, the only difference being a lower yield of 1–2% for the ratio of 1 : 8. The rate curve for the higher gypsum to solvent ratio of 1 : 6 show about 40% lower final yield. These results suggest an optimum gypsum to solvent ratio of about 1 : 10. The run with the higher ratio of gypsum to solvent gave lower final yield, in the region of about 55%; X-ray powder diffraction analysis of this solid showed a very high proportion of syngenite.

From the results found in the preliminary runs for low ammonia concentration and the results given in Figs. 2 and 3, it is concluded that the main factors leading to syngenite formation appear to be: (i) low ammonia concentration in the solvent, (ii) low amount of solvent, (iii) low NaCl proportion in the sylvinite and (iv) high residence time in the reactor.

3.2.3. Variation of reaction temperature

The effects of the reaction temperature on gypsum conversion were studied. Four rate curves were determined at 0, 10, 15 and 20 °C, maintaining the other rate controlling variables at the following values: gypsum to solvent ratio 1 : 10, gypsum to KCl ratio 2 : 3, and the NaCl concentration in the sylvinite at 57%. The results are plotted in Fig. 4. These rate curves are very similar to each other, except for the speed of the reaction and the values of conversion where the curves start to level off. A common characteristic of these curves is

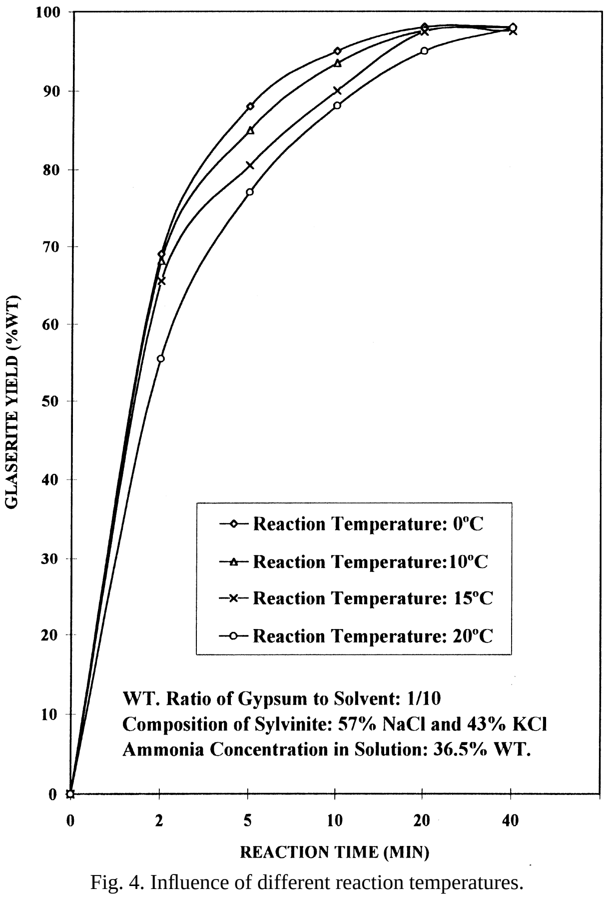

Fig. 4. Influence of different reaction temperatures.

the rapid rate of reaction up to about 20 min, after which the conversions increase very gradually up to about 40 min. Through the entire field of the results, increase in temperature gives an increase in conversion.

3.3. Kinetic model

The reaction under consideration is characterized by the formation of sparingly soluble and readily soluble end products at the surface of an unreacted gypsum core. The solid product remains as a porous ash layer physically attached to the unreacted gypsum; this film porosity changes with time and there is a tendency to slow the reaction. Reactions which undergo retardation as a result of the formation of such films can be described by the following relationship [8,14]:

$$Kt=\frac{X}{X^{*}-X} \tag{5}$$

Rearrangement gives

$$\frac{1}{X}=\frac{1}{KX^{*}}\cdot\frac{1}{t}+\frac{1}{X^{*}} \tag{6}$$

The applicability of Eq. (6) to the rate curves was verified by plotting values of $1/X$ along the abscissa and $1/t$ along the ordinate axis, and with most cases a linear relation was obtained. The value for the retardation factor X^{*} was found to be equivalent to about 98% gypsum conversion for all temperatures, and the values for K varied from 0.2 to 0.9. This model was chosen on the basis of its simplicity.

Experimental values of the overall rate constant, K, were plotted as $\ln K$ against $1/T$ resulting in an equation of the form.

$$\ln K=\left(-\frac{E}{R}\right)\frac{1}{T}+\ln A \tag{7}$$

From this relationship a value for the activation energy of 65 000 kJ/kmol was calculated, suggesting that the formation of glaserite is rate controlled by chemical reaction occurring at the surface of the solid gypsum crystals.

3.4. Form, size and composition of the glaserite crystals

3.4.1. Form and size

SEM photographs of the crystalline products showed clean uniform crystals of similar size, about 10 μm, and similar shape, an hexagonal pyramid.

3.4.2. Composition of glaserite

Glaserite has been shown to have a somewhat variable composition [15,16]. In the present work, chemical and X-ray powder diffraction analysis of the final products, showed compositions very similar to that corresponding to the chemical formula of glaserite $3K_2SO_4\cdot Na_2SO_4$. Some unreacted gypsum was present in the final product, about 1–2%.

3.5. Glaserite conversion to potassium sulphate

3.5.1. General considerations

Equilibrium data for the systems: K_2SO_4–Na_2SO_4–KCl–NaCl–H_2O and K_2SO_4–Na_2SO_4–KCl–NaCl–H_2O–NH_3 have been reported in the literature [17,18], these data reveal that glaserite can be converted with KCl to K_2SO_4 crystals and NaCl in aqueous ammonia according with the following reaction:

$$3K_2SO_4\cdot Na_2SO_4+2KCl \rightarrow 4K_2SO_4\downarrow +2NaCl \tag{8}$$

Glaserite can also be converted to K_2SO_4 in aqueous systems with no ammonia present, but the overall yields are lower [19,20].

3.6. Preliminary experiments on the conversion of glaserite

Preliminary research was conducted following the stoichiometry of Eq. (3) to evaluate the influence on the conversion of glaserite of the variables given below. Values for these variables were fixed on the basis of these runs.

3.6.1. Stirrer speed

The rate of reaction was found to be independent of the speed of agitation above 300 rpm. This speed appeared to be the minimum required to give a uniform suspension in the reactor-crystallizer. A speed of 400 rpm was chosen for all further tests.

3.6.2. Ratio of glaserite to solvent

Four ratios were tested: 1 : 1, 1 : 2, 1 : 3 and 1 : 4. The rate of reaction yield and purity was found to be independent of this variable for values above 1 : 3. This value was chosen for all the experiments.

3.6.3. Residence time

Three residence times were tested: 5, 10 and 20 min. The results showed no significant differences in yield and purity. The effect of this variable was on the crystal size, crystals produced at residence times below 20 min were small and difficult to filter. The value of 20 min was chosen for all further tests.

3.6.4. Sylvinite composition

Trials with sylvinite containing 44, 57 and 63% NaCl showed no significant difference in reaction rate, yield and purity. Sylvinite with 44% NaCl was chosen for further experiments, for convenience.

3.6.5. Excess KCl

Trials with excess KCl of 10, 15 and 20%, above the theoretical value showed complete gypsum conversion for 20% excess KCl, at ammonia concentration of 36% (w/w). If the unconverted gypsum, about 2%, is acceptable in the final product, no excess of KCl is required and the ammonia concentration could be lower, at about 25%.

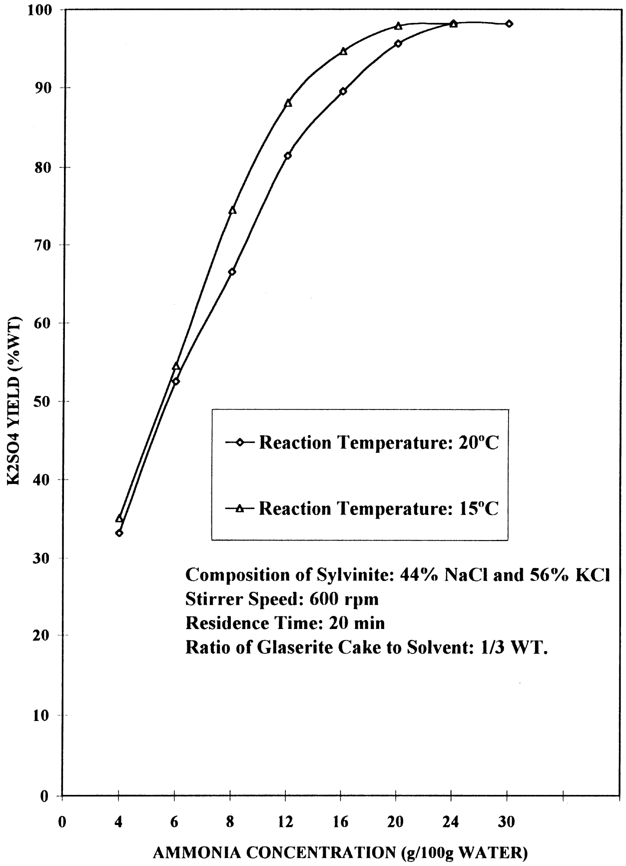

Fig. 5. Relationship between K_2SO_4 yield and ammonia concentration.

Fig. 6. SEM photographs of the K_2SO_4 crystals produced by the ammoniation process.

3.7. Variation of ammonia concentration

The ammonia concentration in solution was found to be the main variable. The effects on the recovery of K_2SO_4 were investigated in the same reactor as that used for the fabrication of glaserite. To follow the course of Eq. (3) the mass of K_2SO_4 crystals formed were weighed at each ammonia concentration in solution. Each run involved a batch crystallization which gave one point in the curve, the results are presented in Fig. 5, showing that over 99% recovery of K_2SO_4 is possible with ammonia concentration of 32 g per 100 g of water. The results for the reaction temperatures of 15 °C and 20 °C followed virtually the same curve.

3.8. Conversion of residual gypsum

It was found that some natural gypsums have low reactivity, which accounts for their incomplete conversion in the first stage [8,9]. Gypsum excess above the theoretical value should be used to reduce potassium chloride losses; the unconverted gypsum will be present in the final product. It has been claimed that a substantial gypsum content in the potassium sulphate is beneficial to the growth of many crops. However, if no gypsum was desired in the final product, this can be realized by conducting the glaserite conversion stage with less than about 20% excess of KCl above the stoichiometric ratios of Eq. (8), at ammonia concentration in solution of about 36% (w/w), and with the other variables kept at values already stated for glaserite conversion. Under these conditions it has been found that the following reaction for unreacted gypsum occurs simultaneously with Eq. (3),

$$CaSO_4 \cdot 2H_2O + 2KCl \cdot XNaCl \leftrightarrow K_2SO_4 \downarrow + CaCl_2 + XNaCl + 2H_2O \qquad (9)$$

3.9. Form and size of the potassium sulphate crystals

SEM photographs of the crystalline products, presented in Fig. 6 show unveiled uniform orthorhombic crystals of similar size, about 350 µm, and similar width and thickness.

4. Conclusions

Glaserite represents a chloride free fertilizer material with about 40% K_2O content. The most promising conditions for possible industrial application are: gypsum produced from seawater bittern of size range 0–62 µm, initial solvent composition 36.5% (w/w) ammonia in water, sodium chloride in the sylvinite 44–63%, weight ratio of gypsum to solvent 1 : 10, reaction temperature 20 °C, after 20 min reaction time the yield of glaserite was about 98%.

Potassium sulphate has been produced by reacting glaserite containing about 2% unconverted gypsum with sylvinite in aqueous ammonia. A range of conditions have been established that gave over 99% recovery. These conditions are: weight ratio of glaserite wet cake to solvent 1 : 3, reaction time 20 min, sodium chloride in the sylvinite 44%, reaction temperature 20 °C and ammonia concentration in the solvent 25% (w/w). The unconverted gypsum present in the glaserite may be converted together with the glaserite to potassium sulphate if the operation is conducted using about 20% excess potassium chloride. The filtrate and washings from this operation may be recycled to the glaserite reactor.

With the respect to the reactor conditions and selected experimental conditions used in this study, the formation of glaserite is rate controlled by chemical reactions occurring at the surface of the solid gypsum crystals. Some of the rate conversion curves are reasonably approximated by an equation of the form

$$\frac{1}{X}=\frac{1}{KX^*}\cdot\frac{1}{t}+\frac{1}{X^*}$$

A first analysis of the data shows the activation energy to be in the region of 65 000 kJ/kmol.

5. Nomenclature

V	volume of liquid in the reactor, ml
X	quantity of reagent converted in time t to glaserite
t	reaction time
X^*	quantity of reagent which should be converted for the film to become impenetrable
K	overall reaction rate constant.

Acknowledgements

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