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K_2SO_4 production via the double decomposition reaction of KCl and phosphogypsum

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Abstract

The production of potassium sulfate from phosphogypsum and potassium chloride in the presence of ammonia and isopropanol has been investigated. The solubility of phosphogypsum in aqueous solutions of KCl, HCl, and mixtures of both has been first measured at various temperatures and concentrations. The factors affecting the conversion of potassium chloride to potassium sulfate, such as aqueous ammonia to phosphogypsum ratio, weight percent of isopropanol in the solution, weight percent excess phosphogypsum, and reaction temperature and pressure have also been investigated.

The optimum reaction conditions obtained at 25°C and atmospheric pressure have been 50% excess phosphogypsum, 4.32 ammonia solution to phosphogypsum ratio, and aqueous solutions containing initial concentrations of 33 wt.% ammonia and 7 wt.% isopropanol. The maximum conversion of KCl to K_2SO_4 obtained under these conditions was 97.2%. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: K_2SO_4 production; Double decomposition; Phosphogypsum process; Phosphogypsum solubility

1. Introduction

Potassium is one of the basic nutrients for plants. It retains water in the plant cells by osmotic pressure that enables the plants to resist weathering and frost, and also contributes to the formation of cellulose, starch and sugar. Potassium is found in soil in insufficient quantities to produce crops of optimum quality, so it must be added to the soil as an essential component in all fertilizers.

Potassium occurs rather frequently in nature. A shortage of mineable potassium minerals is up to now not in sight. The most important water-soluble potassium mineral is potassium chloride with up to 62% K_2O, potassium sulfate with 50% K_2O, and potassium nitrate with 44% K_2O [1]. Fertilizers with potassium chloride are necessarily connected with bringing in chloride ions with large quantities into the soil. But many plants are sensitive to chlorides, among these are many useful crops such as potatoes, tomatoes, red pepper, citrus trees and tobacco. These crops have a special great need for potassium [2]. An additional disadvantage of chlorides is that they, as components of mixed or complex fertilizers, together with ammonium nitrate (the most important fertilizer) form compounds that are of a great hazard to the environment. For these reasons, potassium chloride is converted to chloride-free potassium salts [3].

Potassium sulfate is recommended to be used as a fertilizer instead of potassium chloride because it has the following distinct advantages [4]:

1. It is a two-nutrient fertilizer (K+S), since it contains 50% K_2O and 18% S.
2. It contains a very low amount of chloride.
3. It has a low salt index, so it is better suited for use on saline-sensitive crops.
4. It possesses excellent physical properties and usually is recommended for use in high quality crops.

For these reasons, many processes have been used to convert the potassium chloride, in the presence of a source of sulfate, into potassium sulfate. These processes include the Mannheim process by the reaction of potassium chloride with sulfuric acid, the Glaserite process by the reaction of potassium chloride with sodium sulfate, and the Phosphogypsum process by the reaction of potassium chloride with phosphogypsum in the presence of ammonia and alcohol, and others [5].

Since sulfate reserves are limited and the Phosphogypsum process uses an industrial waste (phosphogypsum) as a source of sulfate, this will drastically reduce the cost of the sulfate component. This process also avoids the production of acid by-products (such as HCl as in the Mannheim process), thus no special materials of construction are needed.

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Furthermore, the use of phosphogypsum will be a valuable contribution to the environment protection. But irrespective of these advantages, this process needs a lot of water for dissolution of the phosphogypsum [5].

The objective of this work is to study the factors that affect the production of potassium sulfate by the Phosphogypsum process in the presence of ammonia and isopropanol. This objective will be achieved by

1. Studying the solubility of phosphogypsum in aqueous solutions containing KCl, HCl, and mixtures of both.
2. Studying the effect of temperature, pressure, excess phosphogypsum, ammonia solution to phosphogypsum ratio, and other parameters on the conversion of KCl to K_2SO_4.

The main reasons behind such a work are

1. The reaction is carried out at ambient conditions, so it does not need heating or cooling.
2. The availability of phosphogypsum and KCl in huge and excess amounts in Jordan.
3. The products of this process are not that highly corrosive when compared to the Mannheim and the solvent extraction processes, for example.
4. The main product (K_2SO_4) can be easily extracted by crystallization in the presence of ammonia.
5. Ammonia and isopropanol used in the reaction can be easily recovered and used for further K_2SO_4 production.

2. The Phosphogypsum process

Potassium sulfate can be produced by the double decomposition reaction of potassium chloride and phosphogypsum in aqueous ammonia solution at low temperatures.

$$2KCl + CaSO_4 \cdot 2H_2O \rightarrow K_2SO_4 + CaCl_2 + 2H_2O \quad (1)$$

The presence of ammonia prevents the formation of complex salts such as syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) and penta-salt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$).

Fernandez and Wint [6] studied the above reaction in the presence of ammonia solution, and found that ammonia has two main actions. These actions are used in two of the principal stages of the process; firstly to induce the reaction between gypsum and potassium chloride to move in the desired direction, and secondly to selectively crystallize the potassium sulfate formed. They carried out the reaction in exact stoichiometric proportions of KCl and gypsum, together with aqueous ammonia to phosphogypsum weight ratio of 4.32. They found that a 98% conversion of KCl to K_2SO_4 could be obtained with a 40 wt.% ammonia in the feed solution for a reaction time of about 1 h and at a reaction temperature of 0°C. They claimed that the K_2SO_4 produced is metastable and has the tendency to be further converted into syngenite.

Fernandez and Wint [7] found that at higher concentrations of ammonia (>36 wt.%), the pressure would rise above atmospheric pressure at the reaction temperatures being investigated. A 97.3% yield of K_2SO_4 from KCl was obtained in 35 min at 30% excess gypsum, 0–104 μm gypsum particles size range, a weight ratio of ammonia solution to gypsum of 9.08, 36 wt.% initial ammonia concentration in the solution, and 15°C.

Goerlich [3] studied the effect of adding methanol to the mixture at ambient temperature. He found that the optimum conversion lies at a methanol content of about 5 wt.%, and at ammonia content near the saturation point. At longer reaction times syngenite is supposedly formed. This points to the fact that ammonia and methanol do not influence the equilibrium itself, but serve as catalysts for the rate of one of the two competing reactions

$$\begin{aligned} &2KCl_{(aq)} + 2CaSO_4 \cdot 2H_2O \\ &\rightarrow K_2SO_4 \cdot CaSO_4 \cdot H_2O\,(\text{syngenite}) + CaCl_{2(aq)} + H_2O \end{aligned} \quad (2)$$

$$\begin{aligned} &2KCl_{(aq)} + CaSO_4 \cdot 2H_2O \overset{NH_3+\text{methanol}}{\rightarrow} K_2SO_4 \\ &\quad + CaCl_{2(aq)} + 2H_2O \end{aligned} \quad (3)$$

Other probable ways for syngenite formation are

$$K_2SO_4 + CaSO_4 \cdot 2H_2O \rightarrow K_2SO_4 \cdot CaSO_4 \cdot H_2O + H_2O \quad (4)$$

$$2K_2SO_4 + CaCl_2 + H_2O \rightarrow K_2SO_4 \cdot CaSO_4 \cdot H_2O + KCl \quad (5)$$

Elkanzi and Wint [8] studied the kinetics of the reaction of gypsum with potassium chloride in aqueous solutions containing 35% ammonia (by weight) under conditions of chemical reaction control. A simple power law model was found to reasonably fit the data and yielded a second-order reaction with respect to potassium chloride with an estimated value for the activation energy of about 49 kJ/mol. Elkanzi and Wint [9] found that the shrinking core model successfully fits the reaction of gypsum with potassium chloride in aqueous solutions containing 35 wt.% ammonia, gypsum particle sizes below 45 μm, KCl concentrations close to saturation and a temperature range of −10 to 0°C. Under these conditions the process was shown to be under chemical rate control with a maximum gypsum conversion of 80%. The energy of activation in this case was estimated to be 58.5 kJ/mol.

Abu-Eishah [10] studied the production of potassium sulfate from potassium chloride and phosphogypsum using aqueous solutions containing 30 wt.% NH_3, and 5 wt.% methanol and found that the optimum condition for 98.5% KCl conversion is −5°C at a residence time of 13.5 min.

The Royal Scientific Society of Jordan [11] studied the production of K_2SO_4 from KCl and phosphogypsum at ambient temperatures and using aqueous solutions containing ammonia and *n*-propanol as a catalyst for the reaction. The optimum conditions that yield 96.1% KCl conversion were 30 wt.% NH_3 and 7 wt.% *n*-propanol initial concentrations, and a residence time of 40 min at 25°C.

Patel and Safya [4] studied the production of K_2SO_4 from KCl and phosphogypsum at 5°C. The optimum conditions that gave about 90% conversion of gypsum were found to be 40 wt.% ammonia solution, a weight ratio of gypsum to KCl of 1:2, a weight ratio of gypsum to ammonia solution of 1:4.5, and 50–120 min reaction time.

3. Role of additives and calculation of KCl conversion

Phosphogypsum, as a by-product obtained in the manufacture of phosphoric acid by the wet process, reacts with potassium chloride to produce potassium sulfate according to Eq. (1). This reaction has been carried out at ambient temperatures in the presence of an aqueous solution containing ammonia and isopropanol.

3.1. Role of ammonia

The presence of ammonia in a solution can sharply reduce the solubility of some inorganic salts in water, while hardly affecting the solubility of other compounds. Ammonia is used in the recovery of KCl from sylvinite (KCl, NaCl), and recovery of K_2SO_4 from aqueous solutions free of or containing NaCl and/or $CaCl_2$ [12]. This action may be attractive industrially in two types of applications [7]:

1. A salt may selectively crystallize by salting out from a solution containing quantities of other salts whose solubilities are relatively unaffected by ammonia.
2. The double decomposition reactions between some salts may be steered in the desired direction, if the solubility of one of the products is reduced by the effect of ammonia such as the reaction of gypsum with KCl and the reaction of ammonium sulfate with KCl.

It has been found that even modest concentrations of dissolved ammonia markedly reduce the solubility of potassium sulfate [6]. There is also an indication that K_2SO_4 recoveries in excess of 99% can be achieved with ammonia solutions exerting an ammonia partial pressure of approximately 1.0 bar (32 kg ammonia per 100 kg of water) at 15–20°C.

In aqueous systems containing no ammonia, gypsum and potassium chloride react to form the syngenite and the penta-salt. These salts subsequently decompose to K_2SO_4, but the overall yields of such processes are disappointing. In the presence of ammonia, the reaction occurs with avoidance of the syngenite intermediate step, and the solubility of K_2SO_4 is markedly reduced [7].

3.2. Role of isopropanol

Some physical properties of *n*-propanol and isopropanol are shown in Table 1 [13]. The presence of isopropanol in aqueous solutions reduces both the solubility and density of the potassium sulfate. Therefore, it tends to crystallize potassium sulfate at ambient temperatures and the obtained crystals are of high purity [14]. The potassium sulfate solubility data in aqueous isopropanol mixtures are shown in Fig. 1.

Table 1
Physical properties of isopropanol and *n*-propanol

Physical property	Isopropanol	*n*-Propanol
Molecular weight	60.1	60.1
Normal boiling point (°C)	82.3	97.2
Freezing point (°C)	−88.5	−126.2
Density at 20°C (g/ml)	0.7849	0.8038
Vapor pressure at 20°C (kPa)	4.4	1.987

3.3. Calculation of KCl conversion

The conversion of KCl to K_2SO_4 from experimental results obtained according to Eq. (1) is represented in terms of

$$X_A = \frac{2 \times \text{moles of } K_2SO_4 \text{ produced}}{\text{moles of KCl charged to the reactor}} \tag{6}$$

where X_A is the KCl conversion at any time. All calculated conversions should have correction factors in order to compensate for the loss of material during sampling [7].

Available data show that while gypsum has a very low solubility in ammonia–water solutions, calcium chloride is just below its saturation level in all experiments [7]. Consequently, analysis for the Ca^{2+} content in the liquid samples withdrawn from the reactor should give direct approximate indication of the progress of the reaction. However, to arrive at a precise value of the conversion at any given state, accurate calcium balance on the reactor contents has to be made. This requires the knowledge of the total volume of the reaction mixture contained in the reactor, *V*, at the time of each sampling. Thus,

$$X_A = \frac{K^+ \text{ equivalent to } Ca^{2+} \text{ content of the sample} \times V}{\text{Total } K^+ \text{ charged to the reactor} \times \text{Volume of the sample}} \tag{7}$$

For each sample, the value of *V* was calculated from the initial liquid volume charged to the reactor (ammonia–alcohol solution), with corrections being made for the following:

1. The water of hydration released from phosphogypsum into the reaction mixture as reaction proceeds.
2. The solution volume is reduced by 5 ml at each sampling time.
3. The presence of dissolved salts (initially KCl, with its gradual replacement by $CaCl_2$) contributes by a small increase in the total liquid volume, *V*.

Two additional sets of small corrections must be made for each value of the conversion:

1. The loss of dissolved $CaCl_2$ from the reactor at each sampling time has to be allowed for in the numerator of Eq. (7) when subsequent samples are analyzed.

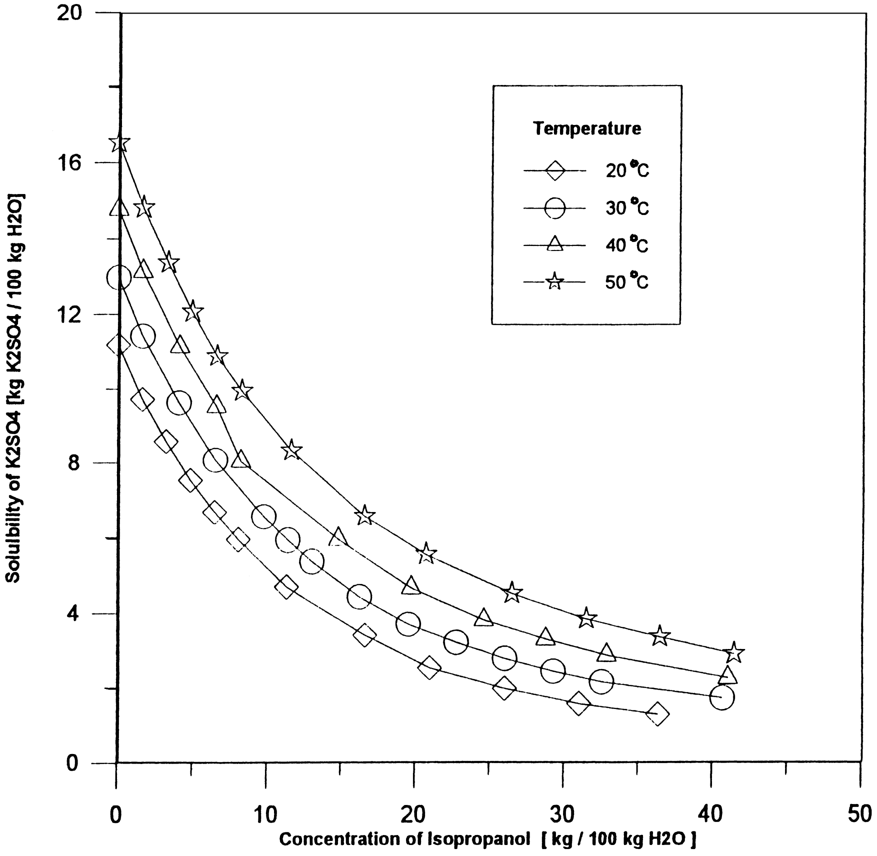

Fig. 1. Solubility of potassium sulfate in aqueous isopropanol as a function of temperature [14].

2. The loss of dissolved KCl from the reactor at each sample has to be subtracted from the denominator of Eq. (7) for subsequent samples in the run [7].

Eq. (7) has been used in this work to calculate the KCl conversion to K_2SO_4 during the course of reaction.

4. Preparatory tests

Two tests have been made before the main reaction has been carried out. These tests are (1) washing of the phosphogypsum, and (2) measurement of the solubility of the washed phosphogypsum in solutions containing KCl, HCl, or mixture of both.

4.1. Washing of phosphogypsum

Phosphogypsum is regarded as a waste by-product in the phosphoric acid production by the wet process. It has very close characteristics to natural gypsum but it contains additional soluble and insoluble impurities that must be removed. Some of these impurities may be removed by simple means, e.g., washing with fresh (tap) water, while others may need complex methods of treatment which tend to be costly. Purification of the phosphogypsum must be achieved before being used in any application. Typical chemical analysis of a sample provided by the Jordan Phosphate Mines Company (JPMC) is given in Table 2.

The washing process has been accomplished as follows: a certain amount of phosphogypsum is taken, dried in an electric oven for 24 h at 105°C, cooled to room temperature inside a dissicator, then ground. A 1 kg of the ground powder is taken and placed in a container, 2 l of tap water is added, and the resulting slurry is thoroughly mixed using a mechanical stirrer for 30 min. The foam formed on the surface of the slurry during mixing is collected. The slurry is filtered and the cake is washed with tap water for three times. The cake from the third wash is dried, ground, and sieved.

Table 2
Dry basis chemical analysis of the phosphogypsum sample before washing (as provided by JPMC) and after 3rd washing

Compound	Before washing (wt.%)	After 3rd washing (wt.%)
Total P_2O_5	2.04	1.98
Acid insoluble residue	3.12	2.78
Loss on ignition (550°C)	6.78	5.3
Loss on ignition (950°C)	8.04	6.07
CaO	34.6	38.0
SO_3	49.68	50.34
Cl	0.0686	0.0177
F	0.83	0.56

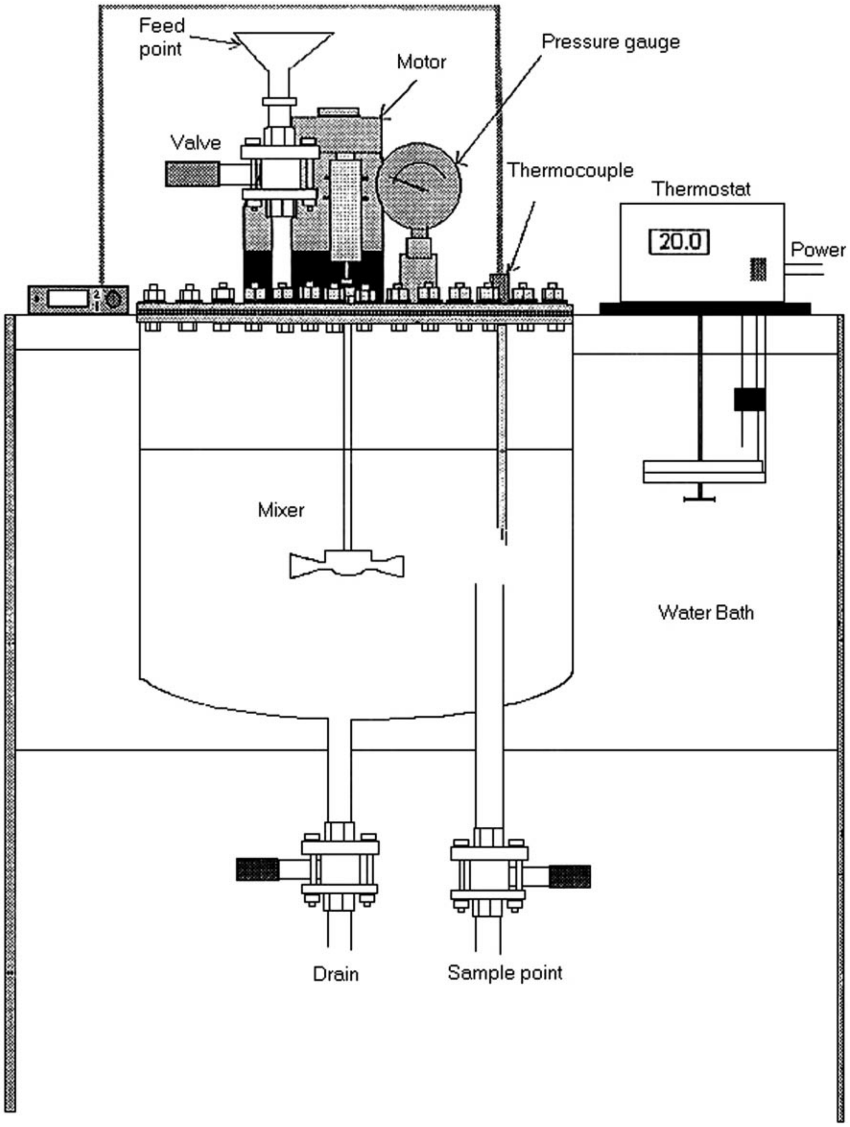

Fig. 2. Experimental setup used in this work for production of potassium sulfate by the Phosphogypsum process.

Typical analysis of the phosphogypsum after the 3rd washing is shown in Table 2. By this repeated washing, the phosphogypsum sample has lost about 2.5% of soluble matter. Thus the purity of the resulting phosphogypsum is about 97.5%. Analyses of tap water as well as water after being used for washing of the cake are shown in Table 3.

Table 3
Analysis of water before and after being used for washing the phosphogypsum sample

Type of water	Ca^{2+} (mg/l)	K^+ (mg/l)	Na^+ (mg/l)	Mg^{2+} (mg/l)
Tap water	229	2.98	41.5	25.8
Water after 1st wash	593	15.36	491.5	37.15
Water after 2nd wash	484	7.70	209	30.1
Water after 3rd wash	410	5.33	108.5	28.65

4.2. Solubility of phosphogypsum in KCl and HCl solutions

A solution of KCl, HCl, or their mixture is prepared in the desired concentration and poured into a beaker. The beaker, with its contents, is placed in a constant-temperature water bath. A certain amount of the previously washed phosphogypsum is added to the beaker and the slurry mixture is then stirred mechanically for 45 min. The resulting slurry is then filtered, and the cake is dried and weighed. The filtrate is then analyzed for the amount of the phosphogypsum dissolved using atomic absorption spectrophotometer (AAS). Typical analyses of the solubility of phosphogypsum in the above-mentioned solutions are presented later.

4.3. Experimental setup

The experimental setup used in this work is shown in Fig. 2. The stirred-batch reactor-crystallizer vessel is manufactured in the Engineering Workshops at the Jordan University of Science and Technology (JUST). It is made of a corrosive-resistant stainless steel 316, cylindrical in the shape (0.2 m internal diameter×0.3 m height), and has a working volume of about 6.0 l.

The reactants can be added to the reactor through a 0.5 in. diameter stainless steel tube, fitted with a funnel and an isolating valve, at the top of the vessel. Agitation of the reaction mixture is carried out with a pitched-blade turbine having four blades at 45° pitches (each is 70 mm long and 25 mm wide) and driven by a variable speed DC motor. The agitator shaft is fitted with a mechanical pressure seal mounted on the top lid of the vessel. Samples of the slurry can be drawn off the reactor via a 0.5 in. diameter stainless steel tube fitted with a valve at the bottom of the vessel. The reactor can be drained through a 0.5 in. stainless steel tube fitted with an isolating valve, at the center of the vessel base. The temperature of the reactor is controlled using a constant-temperature water bath, while the pressure inside the reactor is controlled using nitrogen gas as a purge. Details of the experimental procedure followed in this work are presented elsewhere [15].

5. Results and discussion

5.1. Solubility of phosphogypsum in KCl and HCl solutions

The solubility of the washed phosphogypsum in tap water at 25°C has been determined experimentally to be 1.98 g/l. The solubility of the washed phosphogypsum in aqueous solutions of KCl, HCl, and mixtures of both, is shown in Figs. 3–5. The solubility of phosphogypsum in these solutions is determined as the difference in phosphogypsum weight before and after dissolution divided by the total volume of the solution mixture.

5.1.1. Solubility of phosphogypsum in KCl solution

As shown in Fig. 3, the solubility of the washed phosphogypsum is slightly increased with the increase of the concentration of KCl. This might be due to the reaction between KCl and phosphogypsum, but at higher KCl concentrations the tendency for the double salt formation increases [16]. On the other hand, as the temperature is increased the solubility of the phosphogypsum decreases, due to the increased tendency for the double salt formation.

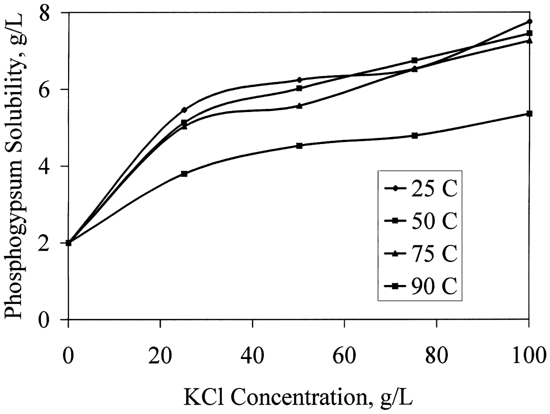

Fig. 3. Effect of temperature on the solubility of phosphogypsum in KCl solution, mixer speed=450 rpm, mixing time=45 min.

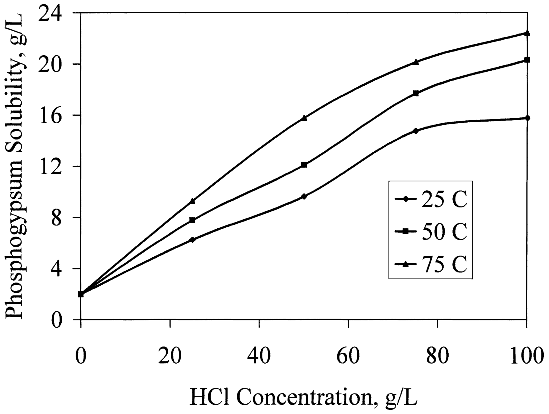

Fig. 4. Effect of temperature on the solubility of phosphogypsum in HCl solution, mixer speed=450 rpm, mixing time=45 min.

5.1.2. Solubility of phosphogypsum in HCl solution

Here the solubility of the washed phosphogypsum is sharply increased as the concentration of HCl is increased (see Fig. 4). This increase in solubility might be due to the affinity of the HCl to dissolve (and react with) phosphogypsum and leave it in ionic form. This affinity also increases with the increase of solution temperature, where the solubility in the 100 g/l HCl solution reached 22.43 g/l at 75°C compared to 15.78 g/l at 25°C.

5.1.3. Solubility of phosphogypsum in a 1:1 KCl to HCl solution

Fig. 5 shows that the solubility of the washed phosphogypsum in 1:1 KCl to HCl solution increases with the increase of the concentration of the KCl–HCl mixture and temperature. This solubility is a midway between the sol-

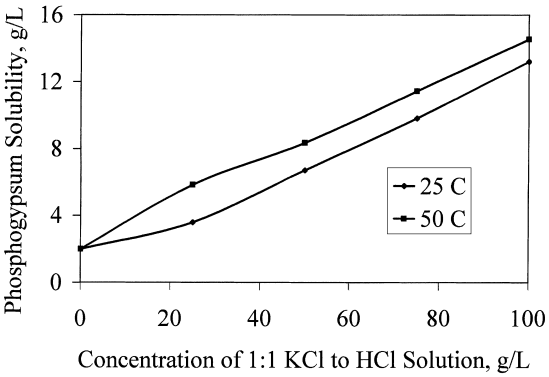

Fig. 5. Effect of temperature on the solubility of phosphogypsum in 1:1 KCl–HCl solution, mixer speed=450 rpm, mixing time=45 min.

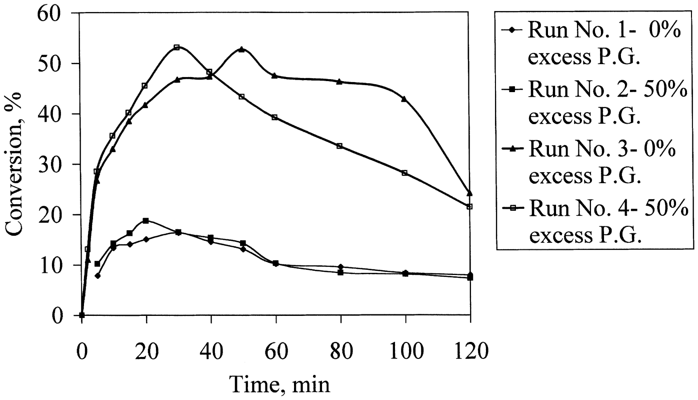

Fig. 6. Production of potassium sulfate from KCl and phosphogypsum (no ammonia, no alcohol for Runs No. 1 and 2), and (33% ammonia, no alcohol, and 4.32:1 ammonia solution to phosphogypsum ratio for Runs No. 3 and 4), at 25°C, 1 atm, and mixer speed=230 rpm.

ubility of phosphogypsum in KCl solution alone and HCl solution alone.

Lastly, it is clear that the washed phosphogypsum has its highest solubility in the HCl solution and its lowest solubility in the KCl solution. It reaches 15.78 g/l at 25°C in 100 g/l HCl solution compared to 13.2 g/l for a 1:1 KCl to HCl solution and 7.76 g/l for KCl solution. In the 1:1 KCl to HCl solution, the presence of HCl increases the solubility of phosphogypsum and decreases the tendency for the double salt formation, while the presence of KCl oppositely increases the tendency for the double salt formation.

5.2. KCl conversion: a parametric study

The conversion of KCl to K_2SO_4 has been first studied at 25°C and 0.0 bar gauge in the absence of ammonia and alcohol in the solution. Fig. 6 shows that the maximum conversion achieved is about 16% in 20 min, after that syngenite formation is started. This is expected because the ammonia is a necessary homogeneous catalyst that shifts the reaction between KCl and phosphogypsum to the right. Next the conversion of KCl to K_2SO_4 has been studied at 25°C and 0.0 bar gauge using a 33 wt.% ammonia solution (with no alcohol). The maximum conversion achieved in this case was about 53% in 23 min (see Fig. 6). All experiments have been carried out at atmospheric pressure (0.0 bar gauge) unless otherwise mentioned. A list of the operating conditions for the kinetic experiments is given in Table 4.

5.2.1. Effect of ammonia solution to phosphogypsum ratio

The effect of the weight ratio of ammonia solution to phosphogypsum is shown in Fig. 7. Three weight ratios have been tried in the initial reactor charge, namely, 3.0, 4.32, and 5.0. In each case, the aqueous solution contains 33 wt.% ammonia and 7 wt.% *n*-propanol, and the reaction temperature is 25°C. The maximum conversion achieved at the above weight ratios are 73.5, 95.2, and 96.7%, respectively. As shown on Fig. 7, the rate of KCl conversion is the highest at the 4.32 weight ratio. For this reason and because it gives acceptable maximum conversion and consumes less ammonia solution, the 4.32 ratio has been selected as a basis for the rest of the experiments.

5.2.2. Effect of excess KCl

The effect of excess KCl on KCl conversion to K_2SO_4 in aqueous solutions containing 33 wt.% ammonia and 7 wt.%

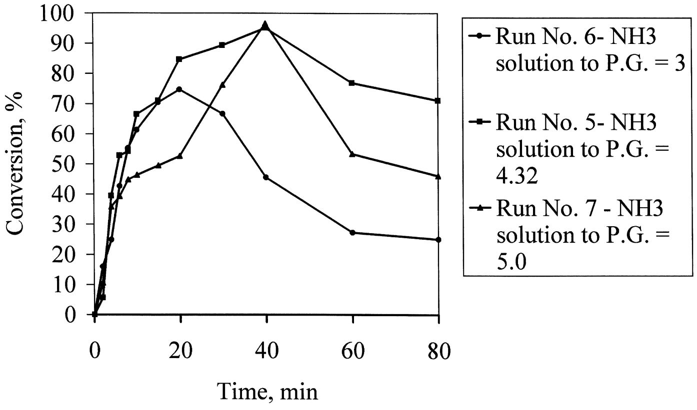

Fig. 7. Effect of ammonia solution to phosphogypsum ratio on the production of potassium sulfate at 25°C, 1 atm, 33% ammonia, 7% *n*-propanol, and mixer speed=230 rpm.

Table 4
Operating conditions for the experiments carried out in this work[a]

Run No.	Temperature (°C)	KCl to PG[b] weight ratio	Ammonia solution to PG[b] weight ratio	Alcohol (wt.%)
1	25	1:1	0% ammonia	0% alcohol
2	25	1:1.5	0% ammonia	0% alcohol
3	25	1:1	4.32:1	0% alcohol
4	25	1:1.5	4.32:1	0% alcohol
6	25	1:1	3.00:1	7% *n*-propanol
5	25	1:1	4.32:1	7% *n*-propanol
7	25	1:1	5.00:1	7% *n*-propanol
5	25	1:1	4.32:1	7% *n*-propanol
8	25	1:0.8	4.32:1	7% *n*-propanol
9	25	1:0.67	4.32:1	7% *n*-propanol
13	15	1:1	4.32:1	7% isopropanol
17	15	1:1.25	4.32:1	7% isopropanol
18	15	1:1.5	4.32:1	7% isopropanol
12	25	1:1	4.32:1	7% isopropanol
16	25	1:1.25	4.32:1	7% isopropanol
11	25	1:1.5	4.32:1	7% isopropanol
14	35	1:1	4.32:1	7% isopropanol
15	35	1:1.25	4.32:1	7% isopropanol
19	35	1:1.5	4.32:1	7% isopropanol
21	25	1:1	4:32:1	5% isopropanol
12	25	1:1	4.32:1	7% isopropanol
20	25	1:1	4.32:1	10% isopropanol
12	25 (0.0 bar)	1:1	4.32:1	7% isopropanol
22	25 (0.5 bar)	1:1	4.32:1	7% isopropanol
23	25 (1.0 bar)	1:1	4.32:1	7% isopropanol

[a] All experiments are carried at 0.0 bar gauge and 33% ammonia by weight in ammonia solution unless otherwise specified.
[b] PG=phosphogypsum.

n-propanol has been investigated at 4.32 ammonia solution to phosphogypsum ratio and 25°C. Fig. 8 shows that as the initial concentration of KCl is decreased below its stoichiometric value the rate of KCl conversion as well as total conversion increases. The maximum conversion reached in this case is 29.2% at 50% excess KCl (1:0.67 KCl to phosphogypsum ratio), 60% at 25% excess KCl (1:0.8 KCl to phosphogypsum ratio), and 95.2% at 0% excess KCl (1:1 KCl to phosphogypsum ratio). This means that the calculated conversion increases as KCl concentration decreases, i.e., as phosphogypsum concentration increases, conversion will increase.

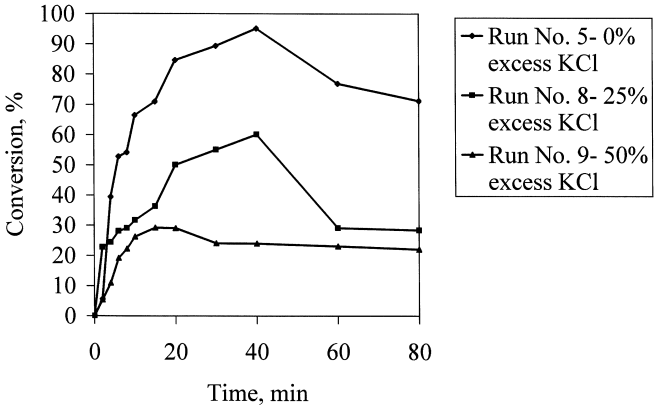

Fig. 8. Effect of excess KCl on the production of potassium sulfate at 25°C, 1 atm, 33% ammonia, 7% *n*-propanol, 4.32:1 ammonia solution to phosphogypsum ratio, and mixer speed=230 rpm.

5.2.3. *Effect of isopropanol concentration*

The effect of the weight percent of isopropanol (in the aqueous ammonia solution) on the conversion of KCl is shown in Fig. 9. The maximum conversion achieved at 10 and 7 wt.% isopropanol are very close (96–98%) and obtained at about 8 min, while using less isopropanol (5 wt.%) only gives 85.4% maximum conversion at about 6 min. As it is also clear in Fig. 9, the tendency for syngenite formation is the lowest at the 7 wt.% isopropanol.

For the rest of the experiments, ammonia solutions containing 33 wt.% ammonia, 7 wt.% isopropanol, and 60 wt.% water has been selected as a basis for the rest of the experiments because it has the highest conversion rate and has an acceptable maximum conversion.

5.2.4. *Effect of pressure*

When the pressure inside the reactor vessel is atmospheric (0.0 bar gauge), i.e. the vessel is open to the atmosphere, the syngenite starts to form as time proceeds. This is because the

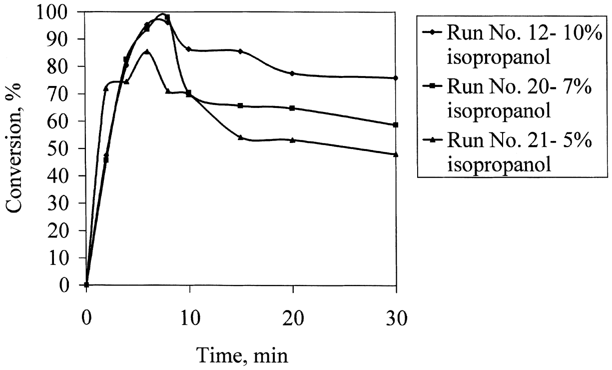

Fig. 9. Effect of isopropanol content on the production of potassium sulfate at 25°C, 1 atm, 33% ammonia, 4.32:1 ammonia solution to phosphogypsum ratio, mixer speed=230 rpm, and 1:1 KCl to phosphogypsum ratio.

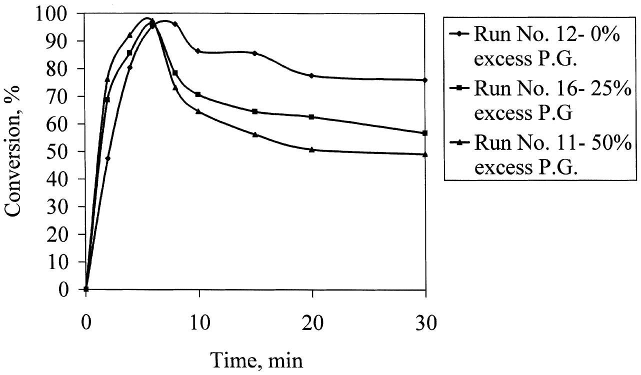

Fig. 11. Effect of excess phosphogypsum on the production of potassium sulfate at 25°C, 1 atm, 33% ammonia, 7% isopropanol, 4.32:1 ammonia solution to phosphogypsum ratio, and mixer speed=230 rpm.

ammonia which is used as a catalyst for the reaction tends to vaporize from the solution and escape to the atmosphere, and thus its concentration will somewhat decrease.

On this basis the effect of pressure on the conversion of KCl to K_2SO_4 at 25°C, and 4.32 weight ratio of ammonia solution to phosphogypsum has been studied. It is clear from Fig. 10 that as the pressure in the reactor is increased above atmospheric, the rate of KCl conversion decreases and the time needed to reach maximum conversion increases. The maximum conversion reaches 96.1% in 8 min at 0.0 bar gauge, 97.1% in 10 min at 0.5 bar gauge, and 97.6% in 12 min at 1.0 bar gauge. Again, the explanation for this is that as the reactor pressure increases, the vapor pressure of the ammonia in the solution as well as its evaporation rate will decrease, and this will delay (and decrease) the tendency for the double-salt formation. But increasing the pressure above atmospheric leads to difficulties in charging the reactor with solid phosphogypsum feed.

5.2.5. Effect of excess phosphogypsum

The effect of excess phosphogypsum on the conversion of KCl to K_2SO_4 at 15, 25, and 35°C has been investigated. It can be seen in Fig. 11, for example, that as the amount of phosphogypsum exceeds its stoichiometric value, the rate of KCl conversion increases and the time required to reaching maximum conversion decreases. The provision for the excess phosphogypsum is to decrease the effects of deposition of the K_2SO_4 crystals on the surface of the remaining phosphogypsum particles, and thus allowing significantly higher final conversions of KCl. On the other hand, excess phosphogypsum increases the tendency of the syngenite formation at early times, which creates great problems such as over-stirring and transportation of slurries in full-scale processes.

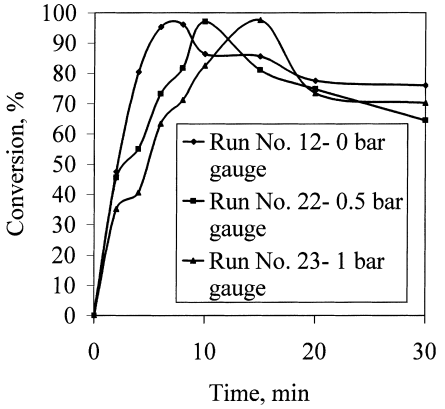

Fig. 10. Effect of pressure on the production of potassium sulfate at 25°C, 33% ammonia, 7% isopropanol, 4.32:1 ammonia solution to phosphogypsum ratio, mixer speed=230 rpm, and 1:1 KCl to phosphogypsum ratio.

It also can be seen from Fig. 11 that the effect of excess phosphogypsum on the maximum conversion of KCl is almost negligible because the reaction takes place only in the liquid phase, which means that only the soluble phosphogypsum reacts with KCl in the solution.

5.2.6. Effect of temperature

The effect of temperature on the conversion of KCl to K_2SO_4 at 15, 25, and 35°C, and 0, 25, and 50% initial excess phosphogypsum has been investigated. It can also be seen in Fig. 12, for example, that as the reaction temperature is increased, the rate of initial conversion of KCl to K_2SO_4 increases, but the final conversion decreases as time proceeds, especially at 35°C, due to the rapid formation of syngenite. This is because as temperature increases, the evaporation rate of ammonia from the reaction solution increases.

On the other hand, Table 5 shows the effect of excess phosphogypsum and temperature on maximum conversion achieved and the time needed to reach that maximum. It is clear that the maximum conversion increases (and the time needed to reach that maximum decreases) with the increase of excess phosphogypsum and decrease of temperature.

An important feature of the studied system is the tendency for the conversion of KCl to fall at high residence times due to the formation of syngenite. From the trend of the results the main factors leading to syngenite formation appear to be: (1) high reaction temperatures, (2) high residence times, (3) low weight ratios of ammonia solution to phosphogypsum,

Table 5
Effect of temperature and excess phosphogypsum on the maximum KCl conversion and the time needed to reach that maximum

Excess phosphogypsum (wt.%)	Maximum KCl conversion, % (Time needed to reach that maximum, min)		
	15°C	25°C	35°C
0	97.4 (8)	96.1 (8)	90.0 (6)
25	97.6 (6)	96.3 (6)	92.4 (4)
50	98.0 (6)	97.2 (6)	92.5 (4)

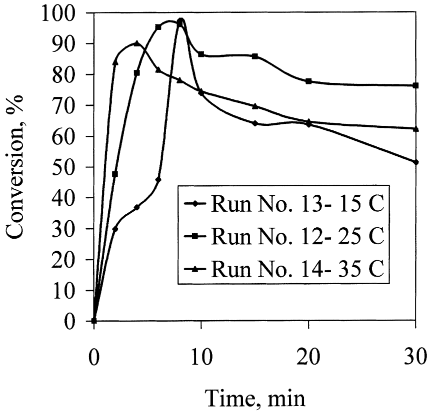

Fig. 12. Effect of temperature on the production of potassium sulfate at 1 atm, 33% ammonia, 7% isopropanol, 4.32:1 ammonia solution to phosphogypsum ratio, mixer speed=230 rpm, and 1:1 KCl to phosphogypsum ratio.

and (4) low weight percent of isopropanol in the solution. Factors (2) and (3) lead to the supposition that the concentration of $CaCl_2$ in the reactor liquid is of high importance because it increases with the decrease of the amount of the solution and also as the reaction progresses [7].

6. Conclusions and recommendations

Based on the results of this work, the following conclusions are applicable:

1. The solubility of phosphogypsum has been found to increase with the increase of KCl and HCl concentration in their solutions and with the decrease of the solution temperature.
2. The conversion of KCl to K_2SO_4 increases with increase of each of the following parameters: weight ratio of ammonia solution to phosphogypsum, weight percent of isopropanol in the solution, excess phosphogypsum, and pressure. The optimum reaction conditions at 25°C and atmospheric pressure are: 4.32 weight ratio of ammonia solution to phosphogypsum, 50% excess phosphogypsum, and 7 wt.% isopropanol in the solution, at which the maximum conversion of KCl to K_2SO_4 was 97.2%.
3. An important feature of the studied system is the tendency for the conversion of KCl to fall at high residence times due to the formation of syngenite. From the trend of the results the main factors leading to syngenite formation appear to be: (1) high reaction temperatures, (2) high residence times, (3) low weight ratios of ammonia solution to phosphogypsum, and (4) low weight percent of isopropanol in the solution. Factors (2) and (3) lead to the supposition that the concentration of $CaCl_2$ in the reactor liquid is of high importance because it increases with the decrease of the amount of the solution and also as the reaction progresses [7].

Lastly, it is recommended to study the reaction conditions under continuous operation, which might need a small pilot plant. It is also recommended to study in depth the reaction kinetics and mechanism, which will be the subject of a future paper in this field.

7. Nomenclature

V	volume of reaction mixture (l)
X_A	conversion of KCl to K_2SO_4

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