

# Production of Potassium Sulphate from Calcium Sulphate and Sylvite or Sylvinite in the Presence of Aqueous Ammoniacal Hydrazine

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## ABSTRACT

Experimental work is reported on the ability of ternary solutions of hydrazine, ammonia and water to promote the reaction of gypsum and potassium chloride to form potassium sulphate. A range of conditions has been investigated, some giving 98% yields of  $K_2SO_4$  with a reactor residence time of about 10 minutes.

The ternary liquid has advantages over previously known additives for promoting this reaction. It is highly effective at ambient temperatures where it has a saturated vapour pressure below one atmosphere, thus reducing the problems of designing solid feed systems to the reactor.

A particularly promising aspect is that good yields are obtained

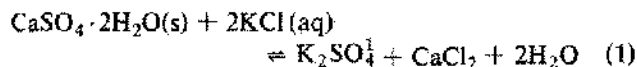
from KCl contaminated with large amounts of NaCl (like sylvinites) as well as from pure KCl (sylvite). As the world's sources of sylvite become depleted, processes based on contaminated material will gain in importance. With sylvinites, the reaction produces glaserite  $3K_2SO_4 \cdot Na_2SO_4$ , a previously unknown step. From glaserite, virtually pure  $K_2SO_4$  can be obtained with a high overall yield from the potassium content of the sylvinites.

The process has potential attractions, especially where calcium sulphate is available as a by-product, when conversion of the sulphate content to high purity  $K_2SO_4$  for use as a fertiliser may bring extra profitability.

## INTRODUCTION

Potassium sulphate is a fertiliser with high nutrient content, which is expected to maintain a healthy long-term position in world fertiliser markets. At present it is usually manufactured by the double decomposition of potassium chloride and one of a number of double salts which contain magnesium sulphate, such as langbeinite  $K_2SO_4 \cdot 2MgSO_4$  or kainite  $KCl \cdot MgSO_4 \cdot 3H_2O$  (Dancy and Stanley, 1959; Henne and Ratsch, 1965; Marrullo, et al. 1965; Noyes, 1966; and Portillo, 1976). However, while potassium chloride is relatively abundant, sources of magnesium sulphate are dwindling. In order to continue production of potassium sulphate, new raw materials must be found to supply the sulphate content. The research described here concerns the possible use of calcium sulphate. This would be attractive commercially as a feed material because of its role as a byproduct from seawater sodium chloride plants, from phosphoric acid plants and from limestone scrubbing systems, which remove  $SO_2$  from combustion tail gases as a pollution

avoidance measure. Alternatively, gypsum is widely available as a natural raw material.



A considerable amount of research work on the production of potassium sulphate from gypsum and potassium chloride has already been reported. (Hadzeriga, 1960; Lamp, 1965; Hamadeit and Perlmutter; Schnabel et al. 1968; Aleksandrov, 1963; Scherzberg, 1965; and Emons and Brantigam, 1967). Solubility studies at 25°C of the system  $CaSO_4 \cdot KCl \cdot K_2SO_4 \cdot CaCl_2 \cdot H_2O$  (van't Hoff, 1912; D'Ans, 1933; and Sweschnikowa, 1949) show that the natural end product of the double decomposition reaction is syngenite  $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ . Any  $K_2SO_4$  formed by equation 1 is only a metastable product. If the system is allowed to progress to the formation of syngenite, severe handling difficulties occur due to the thickening of process liquors. In addition, it is not easy to treat syngenite in order to obtain recovery of the  $K_2SO_4$  content.

Previous research has shown that good yields of  $K_2SO_4$  can be obtained by equation if the reaction is carried out in aqueous ammonia (Lafont, 1959; Nather and Emons, 1969; Fernandez-Lozano, 1980; and Fernandez-Lozano and Wint, 1979 and 1982) or aqueous hydrazine (Emons, 1967; and Emons and Brantigam, 1968). These additives appear not only to promote the formation of solid  $K_2SO_4$  but also to prevent the system moving toward syngenite. However, the use of aqueous ammonia tends to suffer from the disadvantage of the high volatility of ammonia in solution. At the concentrations of ammonia needed to suppress the formation of syngenite, the vapour pressure is substantial. Operating pressures above one atmosphere would bring severe practical difficulties in maintaining a gas-tight seal while feeding solid gypsum. To avoid this, operation at temperatures below ambient has often been recommended, in spite of the added cost. On the other hand, hydrazine solutions do not exert high vapour pressures. Therefore,  $K_2SO_4$  plants based on hydrazine could operate at ambient temperature without difficulty. Nevertheless, high ratios of aqueous hydrazine to gypsum would be needed in the reactor feed stream in order to obtain good conversions, causing high treatment costs. An additional cause for concern would be the tendency of hydrazine solutions to decompose.

The experiments described in this paper feature a new proposal for the liquid charged to the reactor in order to promote the formation of  $K_2SO_4$  and suppress that of syngenite. Ternary solutions of ammonia-hydrazine-water of several compositions have been used and very good yields of  $K_2SO_4$  have resulted. The practical advantages of these ternary solutions over the alternative binary solutions are as follows:

1. The vapour pressure is substantially lower than that of aqueous ammonia, so that a process could be operated at ambient temperatures without the pressure exceeding one atmosphere; the problems associated with a solid feed stream would be substantially eased.
2. The presence of ammonia would inhibit the decomposition of hydrazine.

The results presented form part of a wider study (Fernandez-Lozano, 1980) of several alternative processes for converting gypsum to potassium sulphate.

### Theory of New Ternary Additive

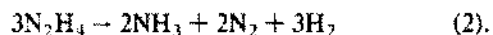
Hydrazine and ammonia belong to the saturated hydro-nitrogen series of compounds with the general formula  $N_nH_{n+2}$ . In fact hydrazine can be regarded as an ammonia derivative in which one of the hydrogen atoms has been replaced by the more negative  $NH_2$  group. Thus hydrazine is a weaker base than ammonia. (Audrieth and Ackerson, 1951). While ammonia has been characterized as the most water-like solvent among both organic and inorganic compounds, hydrazine can be considered as the

second most water-like solvent. Certainly water, hydrazine and ammonia are miscible in all proportions.

Hydrazine, like ammonia, has a free pair of unshared electrons and shows a marked coordinating effect on ions in solution. Both compounds are thus classed as Lewis bases.

Hydrazine and its solutions in water, unlike ammonia and its aqueous solutions, have low vapour pressures (Clark, 1953). In fact, anhydrous hydrazine is of lower volatility than water, boiling under atmospheric pressure at  $113.5^\circ C$ .

Unlike ammonia, hydrazine tends to undergo autoxidation in water, yielding some hydrogen peroxide initially. However, the nature of the final products of the decomposition varies according to the pH of the solution. There is also a tendency for decomposition to occur according to the reaction



However, the decomposition can be prevented by storage under nitrogen or by the presence of ammonia (as in the research being described).

Previous studies have been made (Fernandez-Lozano, 1980; and Fernandez-Lozano and Wint, 1982) of the formation of  $K_2SO_4$  from gypsum and potassium chloride in the presence firstly of aqueous ammonia and secondly of aqueous hydrazine. Rates of formation and yields were higher with the solution of ammonia than with solutions of hydrazine in comparable conditions. In addition it was clear that ammonia was more effective than hydrazine in acting as a stabilizing agent for the metastable system having  $K_2SO_4$  as the solid phase, instead of the undesirable stable end product, syngenite  $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ . Nevertheless, the authors considered that it might be advantageous to replace part of the ammonia content of the additive with hydrazine, thus forming the ternary solution of hydrazine-ammonia-water. If this were shown to be effective in promoting the formation of  $K_2SO_4$  by equation (1), it would bring the major advantage for possible adaption to a commercial process of lowering the total vapour pressure of the solution under ambient temperatures to a value under one atmosphere. Thus the problems of designing a solid feed system would be greatly lessened and predicted vapour losses from the plant would be reduced.

### EXPERIMENTAL

#### Apparatus

The main item of equipment used in this research was a stirred batch reactor-crystalliser. It has been described in detail in a previous paper. (Fernandez-Lozano and Wint, 1982). Therefore, only the chief features will be mentioned here. The reactor was a cylinder of 100 mm internal diameter and 130 mm height, designed to contain a working slurry volume of about 350 ml. This value was a com-

promise between a small volume, which would reduce the consumption of chemicals during the research programme, and a larger vessel that would lessen the effects of removing samples during a test run. In fact, the withdrawal of a maximum of ten samples, each causing a removal of 2 ml of liquid, would result in a reduction of 5.7% of the total reactor liquid during the course of a run.

The samples were obtained via a 2 mm tube fitted with a medium porosity glass filter to prevent the withdrawal of solids. At each sampling a one-milliliter pipette was filled twice, once for flushing purposes, then once for analysis. As described later, this analysis of the clear liquid formed the basis of the method used to follow the course of the reaction. As a check at the end of each run, the solid in the reactor was washed, dried and analysed.

The reaction vessel was stirred by means of a pitched-blade turbine having four blades at 45° pitch, each 47 mm long and 8 mm wide. The rotational speed of 400 rev/min had been shown by previous tests to be well above the minimum necessary to give a uniform dispersion of the gypsum particles in the reactor. Two vertical baffles each 11 mm wide were installed to aid mixing of the reactor contents. The agitator shaft was fitted with a mechanical pressure seal in the vessel lid.

In order to minimise evaporation losses of ammonia, water or hydrazine from solutions or slurries fed to the reactor, a second stirred vessel was used as an injection device. Like the reactor it was connected with a source of compressed air, enabling transfer to be made under pressure. Both the injection vessel and the reactor were maintained at constant temperature by a circulating coolant supplied from a reservoir.

### Procedure

When the reactor and the injection vessel had reached the desired temperature, a weighed amount of the solid potassium chloride source material (sylvite or sylvinite) was introduced to the reactor via a charge port. Then an appropriate weighed amount of gypsum with 350 ml of hydrazine-ammonia-water (referred to as the solvent) were charged to the injector. After a period of stirring, enabling the temperature to reach the desired value, the slurry of gypsum and solvent was transferred to the reactor for the reaction to start. Stirring of the reactor was maintained at 400 rev/min. The course of the reaction was followed by means of samples of liquid, analysed for calcium content by titration with EDTA, using murexide as indicator.

Preliminary tests had been undertaken to establish some of the conditions necessary for a consistently good reactor performance. These conditions were used throughout the series of test runs reported here. As previously mentioned, the stirrer speed was maintained at 400 rev/min. Initial trials with two batches of KCl of different particle size distributions showed no significant difference in reaction rate. (This was expected since KCl is readily

soluble in the ternary solutions used). The particle size distribution of KCl used in all further runs is given in the next section, in addition to that of the NaCl which was used in a few of the tests.

The particle size distributions of the two forms of gypsum used in the tests are detailed in the next section. In almost all the experimental runs, the gypsum and KCl quantities charged to the reactor were in the stoichiometric ratio of equation 1. The only exception to this was in a test with a high proportion of NaCl present in the KCl feed; in this case excess gypsum was added beyond the amount calculated on the stoichiometric ratio with KCl alone.

The preliminary tests had shown that a significant increase in both initial reaction rate and final yield were obtained when the gypsum was added to the hydrazine-ammonia-water solution before the KCl particles, rather than after. This procedure was therefore adopted throughout the test runs. In contrast, the addition of a small quantity of  $K_2SO_4$  crystals to the reaction mixture had no measurable 'seeding' effect on the reaction rate. It was concluded that nucleation of  $K_2SO_4$  was not a rate-determining factor.

The following five variables were found to exert a considerable influence on the course of the reaction:

1. initial composition of the hydrazine-ammonia-water solvent
2. ratio of gypsum to ternary solvent in the reactor charge
3. type of gypsum
4. percentage of NaCl present in the KCl feed
5. reactor temperature.

Information on the range of these variables that were studied and their effects on the reaction is considered in the section entitled "Results."

### Raw Materials

The reactants chiefly used in these investigations were natural gypsum from a mine near Nottingham of purity 98.25% by weight, milled to pass through a 104  $\mu$ m sieve, and analytical reagent KCl of purity 99.5% by weight. Sieve analyses of these materials are presented in Table 1. Also shown is the size analysis of the analytical reagent NaCl, purity 99.5% by weight, which was added to the KCl feed in three experimental runs to simulate the use of sylvinite of three different KCl-NaCl compositions.

A few runs were carried out, not with natural gypsum, but with gypsum supplied as a laboratory reagent, of purity 99.0%. It is designated in this paper as artificial gypsum. Size distribution data, measured by an Andreasson sedimentation test, are given in Table 2. It was hoped that the results obtained from the reactor with artificial gypsum would be a good indication of the likely behaviour of gypsum available as a by-product from flue gas lime-scrubbing treatments or seawater sodium chloride plants.

TABLE 1  
Sieve Data of Chief Raw Materials

Sieve Aperture $\mu\text{m}$	Cumulative Weight Oversize, %		
	Natural Gypsum	KCl	NaCl
599	0	0	0.3
355	0	9.0	44.2
300	0	17.8	63.8
250	0	33.4	81.8
210	0	49.8	92.5
180	0	65.7	96.7
125	0	88.7	99.4
104	0	95.0	99.7
89	19.4	97.1	100.0
76	10.3	97.2	100.0
63	34.2	99.3	100.0
53	9.7	99.6	100.0
45	10.3	99.8	100.0
Pan	16.1	100.0	100.0

TABLE 2  
Size Distribution Data of Artificial Gypsum, by Andreason  
Sedimentation Test

Size, $\mu\text{m}$	Cumulative Weight Undersize, %
100.0	100.0
62.5	95.0
43.7	61.8
30.5	26.0
20.3	9.6
15.5	8.8

Such gypsum may be the cheapest feedstock for a full-scale application of this process.

As described in the Results section, experimental runs were carried out with hydrazine-ammonia-water solutions of three different compositions. These were made up by mixing appropriate amounts of hydrazine hydrate  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  and an aqueous ammonia solution in water containing 36% by weight  $\text{NH}_3$ .

### CALCULATIONS

An economic analysis of the process will show that it is important to achieve a high yield of  $\text{K}_2\text{SO}_4$  from the more expensive reactant KCl. Therefore, the experimental results obtained from the reactor have been presented in terms of

$$\text{yield} = \frac{2 \times \text{kmol of } \text{K}_2\text{SO}_4 \text{ produced}}{\text{kmol of KCl charged to reactor}} \quad (3).$$

All these results have had correction factors applied to them to compensate for the loss of material during the sampling procedure. Thus the results indicate the yields to be expected from a batch reactor operated without withdrawal of samples.

While gypsum has a very low solubility in hydrazine-ammonia-water solutions, calcium chloride is well below its saturation level in all the experiments reported here. Thus analysis for Ca content in the samples of liquid withdrawn from the reactor gives a direct indication of the approximate progress of the reaction. However, to arrive at a precise value of the yield at any given time, an accurate calcium balance on the reactor contents has to be calculated. This requires a knowledge of the total liquid volume  $V$  ml contained within the reactor at the time of each sample. Equation (3) becomes

$$\text{yield} = \frac{\text{K equivalent to Ca content of 1 ml sample} \times V}{\text{total K charged to reactor}} \quad (4).$$

At each sampling,  $V$  was calculated from the initial liquid charge of water and ammonia, with corrections being made for the amount of water released into the mixture as the reaction proceeded and also for the subtraction of 2 ml of liquid at each sampling. Obviously the first of these corrections depended on the progress of the reaction, which could only be calculated precisely by inserting the value of  $V$  in equation (4). Therefore, an iterative procedure was necessary. The details of the adopted method have already been described (Fernandez-Lozano and Wint, 1982). At no time were more than two iterations needed to establish the yield to within 0.1% accuracy.

The validity of this method of calculating values of yield from liquid samples was checked by repeating some of the runs without removal of samples. From these runs the final yields could be obtained directly from the weight and analysis of the solid products. In all these cases the values of yield agreed with those derived from liquid samples to within 3%. Usually the disparity was smaller than 1%.

### RESULTS

#### Variation of Solvent Composition

Three runs were performed to make a rough assessment of the effects on the reaction of changes in composition of the ternary solvent. The compositions (by weight fraction) were

- a) 55.23%  $\text{H}_2\text{O}$ , 21.56%  $\text{N}_2\text{H}_4$ , 23.21%  $\text{NH}_3$
- b) 51.52%  $\text{H}_2\text{O}$ , 29.74%  $\text{N}_2\text{H}_4$ , 18.74%  $\text{NH}_3$
- c) 47.38%  $\text{H}_2\text{O}$ , 38.88%  $\text{N}_2\text{H}_4$ , 13.74%  $\text{NH}_3$ .

All other variables in the system were maintained at constant values; an initial weight ratio of gypsum to solvent of 1:5.54 was used in each run, the solids were natural gypsum and KCl in stoichiometric ratio according to equation (1) and the reactor temperature was held at  $20^\circ\text{C}$  throughout. The results are shown in Figure 1, in which the yield of potassium sulphate from potassium chloride is plotted against time for each of the three runs.

The plots show a rapid increase in the yields obtained up to a residence time of about 10 minutes. Beyond this time

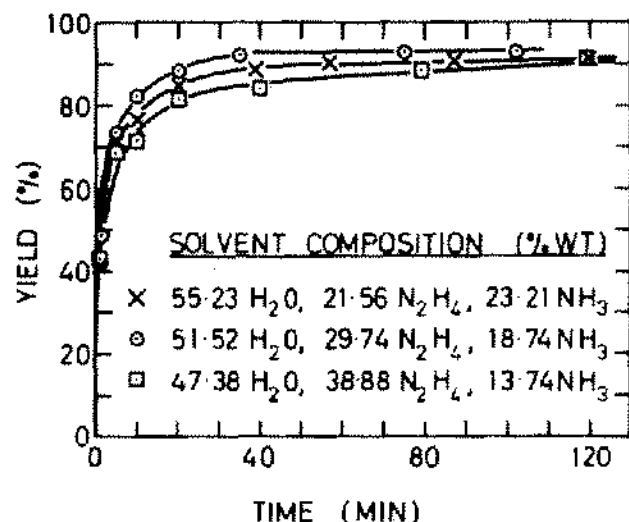


Figure 1. Influence of different solvent compositions.

the rates of conversion slowed. The highest value of yield occurred in the region of 50 minutes with the second solvent composition (b), namely 93%. The other two solvent compositions each gave maximum yields of approximately 91.5%. An interesting feature of these curves is their tendency toward the same values of yield at high residence times. In the presence of substantial concentrations of hydrazine and ammonia, it seems that the metastable solid phase  $K_2SO_4$  is highly stable. The levelling off in reaction rate prior to complete conversion can probably be attributed to the formation of an impervious film of solid  $K_2SO_4$  around the remaining gypsum particles.

The values of reaction yield obtained in the presence of solvent (b) were generally 6.5% to 7% higher than those reported in the presence of 51.52% by weight aqueous hydrazine in equivalent conditions (Fernandez-Lozano, 1980). In terms both of the initial rate of conversion and of yield, solvent (b) was more effective than the other two mixtures investigated. Therefore, it was decided to complete the remainder of the experimental programme using this solvent for all runs.

#### Variation of the Gypsum to Solvent Ratio

The effects on the reaction of changing the amount of the hydrazine-ammonia-water solvent in the reactor feeds were investigated by four further runs. The conditions were identical to those described in the previous section in the experimental run with solvent (b), containing 51.52%  $H_2O$ , 29.74%  $N_2H_4$  and 18.74%  $NH_3$  by weight. In that run an initial weight ratio of gypsum to solvent of 1:5.54 was used. The four additional experiments used ratios of 1:6.65, 1:10, 1:12 and 1:14, respectively. Figure 2 shows the results as yield of potassium sulphate from potassium chloride plotted against time.

The results show higher initial conversion rates when

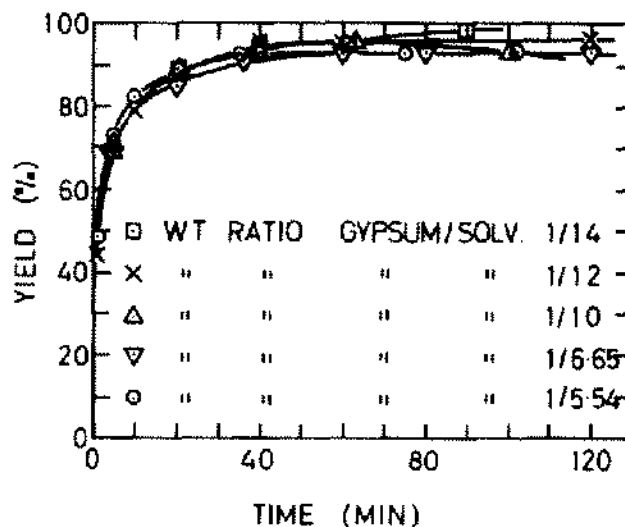


Figure 2. Effects of different gypsum to solvent ratios.

the two lesser amounts of solvent were used. However, as the ratio of solvent to gypsum was increased, the yield continued to grow with residence time. With a solvent input of 14 times the gypsum feed (by weight ratio), a yield of 99.2% was obtained at a residence time of about 90 minutes.

#### Use of Artificial Gypsum

For purposes of comparison with natural (mined) gypsum, two additional runs were carried out with artificial (laboratory reagent) gypsum. The reactor conditions were identical with two of the runs described in the previous section, with results included in Figure 2. Stoichiometric quantities of gypsum and KCl were used, the reactor temperature was 20°C, the solvent composition was by weight 51.52%  $H_2O$ , 29.74%  $N_2H_4$  and 18.74%  $NH_3$ , and the gypsum to solvent ratio was firstly 1:5.54 and secondly 1:12. Figure 3 shows the results of the two additional runs with artificial gypsum, together with the equivalent results for natural gypsum already presented in Figure 2.

Figure 3 shows clearly that much higher initial rates of conversion were obtained with the artificial gypsum. Yields of approximately 98% were indicated after 10 minutes, whereas the equivalent runs for natural gypsum gave yields of only about 80% at that time. The two runs with artificial gypsum showed virtually identical results up to 22 minutes. However, after this time the yield decreased significantly for the run with the lower quantity of ternary solvent. This was inadequate to ensure the stability of the metastable  $K_2SO_4$ , and so some of the double salt syn-genite  $K_2SO_4 \cdot CaSO_4 \cdot H_2O$  was allowed to form.

Figure 3 demonstrates the advantage of using artificial gypsum over natural gypsum. It gives promise of becoming the basis of a commercially viable process, especially

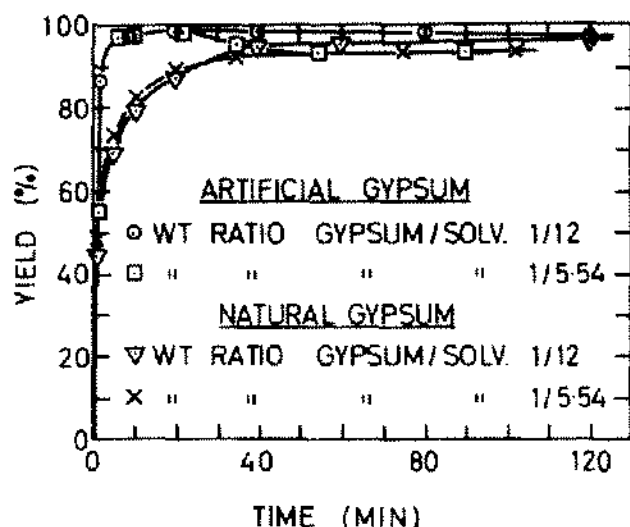


Figure 3. Effects of different types of gypsum.

if, as anticipated, unwanted byproduct gypsums from existing processes behave in a similar manner to the artificial gypsum tested here. It is likely that the smaller particle sizes of the artificial gypsum were important in leading to the higher initial conversion rates than those obtained with natural gypsum.

A comparison of the results portrayed in Figure 3 with those obtained from comparable runs with a hydrazine-water solvent (Fernandez-Lozano, 1980) favours strongly ternary solvent that gives higher initial conversion rates and final yields increased by about 16%. Several factors may be involved in this, for example, the higher solubility of gypsum in the ternary solvent and the higher rate of diffusion through it of  $K^+$  ions.

#### Variation of Reactor Temperature

A total of six experimental runs were performed to assess the effect of temperature on the reaction. Using a gypsum-to-solvent ratio of firstly 1 to 5.54, then 1 to 12, runs were carried out at 20°, 10° and 0°C, respectively. In all these runs, natural gypsum was used, in stoichiometric ratio with KCl and with a ternary solvent of composition by weight 51.52%  $H_2O$ , 29.74%  $N_2H_4$  and 18.74%  $NH_3$ . The results are shown in Figures 4 and 5.

All the curves show yields increasing appreciably with residence time up to about 40 minutes, after which further conversion is relatively slow. In both figures, conversion appears to stop after about 70 minutes, possibly due to the deposition of solid  $K_2SO_4$  product around the remaining particles of gypsum. The results indicate clearly that the highest of these temperatures, 20°C, is to be preferred to the lower alternatives, particularly in view of the lower residence time necessary to achieve a good value of yield. In terms of a full-scale plant lower residence time implies a

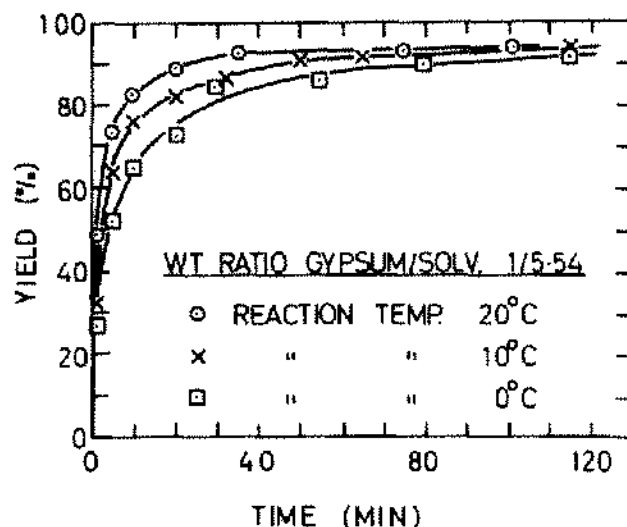


Figure 4. Influence of temperature at a high gypsum to solvent ratio.

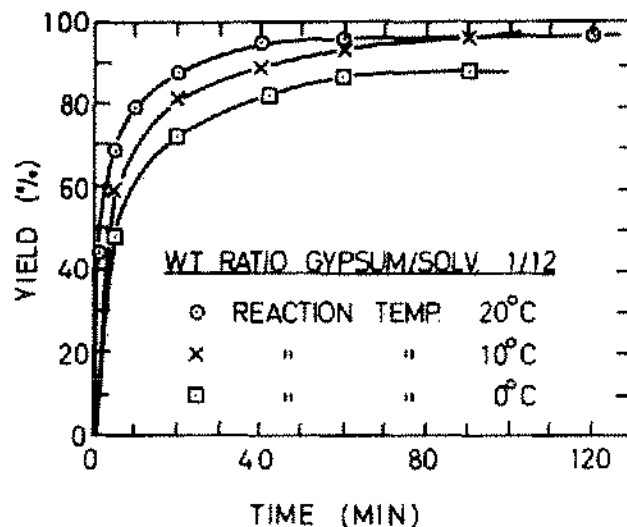


Figure 5. Influence of temperature at a low gypsum to solvent ratio.

significant reduction of reactor volume and hence of capital cost.

#### Presence of NaCl with KCl

In order to assess the effects on the reaction of the possibility of NaCl being present in the KCl feed, three runs were carried out at different KCl-NaCl compositions. The three mixtures tested contained by weight 28.27% NaCl, 44.20% NaCl and 60.53% NaCl, respectively. The runs with the first two of these mixtures used gypsum in exact stoichiometric ratio with the KCl present, according to equation (1). In order to make the third run more realistic

in terms of possible industrial application, the gypsum in this run was considerably in excess of the stoichiometric requirement of KCl alone (in fact 31.52% excess was used). In each of these three runs natural gypsum was used, the reactor temperature was maintained at 20°C, the ternary solvent composition was 51.52% H<sub>2</sub>O, 29.74% N<sub>2</sub>H<sub>4</sub> and 18.74% NH<sub>3</sub> by weight and a gypsum-to-solvent ratio of 1:12 by weight was used.

Analysis of the solid product remaining in the reactor at the end of each run showed that a small but significant proportion of the NaCl reacted with the gypsum to form Na<sub>2</sub>SO<sub>4</sub>, in a similar fashion to the reaction of KCl by equation (1). Under these conditions analysis for Ca of the liquid samples withdrawn from the reactor does not give a measure of the yield of K<sub>2</sub>SO<sub>4</sub> alone. Instead, therefore, the results based on these analyses are given in Figure 6 as gypsum conversion plotted against time. A curve corresponding to an earlier run in comparable conditions with no NaCl present is also shown.

The plots show that the presence of NaCl leads to an increased rate of gypsum conversion at low residence times. However, there appears to be little difference in gypsum

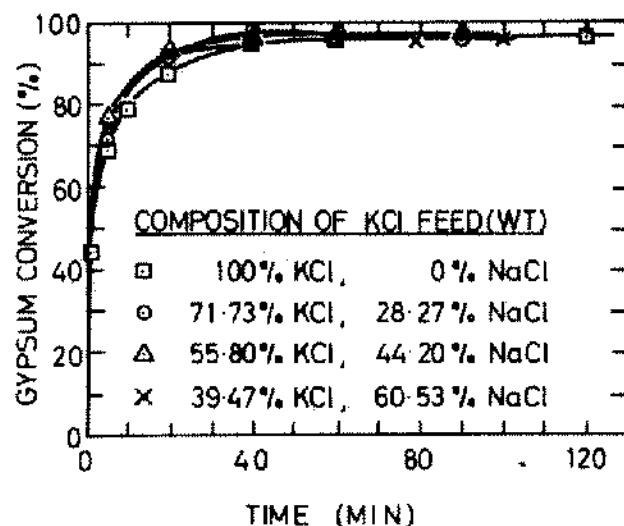


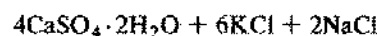
Figure 6. Effects on gypsum conversion of different proportions of NaCl in the KCl feed.

conversions at higher residence times. The rate curve for the conversion of gypsum with KCl containing 60.53% NaCl and with 31.52% excess gypsum is almost identical to the rate curve obtained for KCl containing 44.20% NaCl but with no excess gypsum. This suggests the possibility that the reaction is rate controlled by chemical reaction at the surface of the gypsum particles and that the levelling off in the reaction rate prior to complete conversion is due to the formation of an impenetrable film of 3K<sub>2</sub>SO<sub>4</sub>·Na<sub>2</sub>SO<sub>4</sub> on the surface of the untreated gypsum.

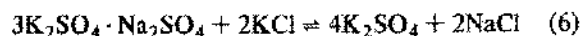
The results of the analyses of the solid products remaining in the reactor at the end of each run are presented in Table 3. Also shown are the final conversion figures for the KCl, NaCl and gypsum charged to each run. It is clear that as the NaCl in the feed KCl was stepped up, the proportion of Na<sub>2</sub>SO<sub>4</sub> in the solid product showed a roughly similar increase.

It is worth noting that in the run with 60.53% NaCl in the KCl feed and 31.52% excess gypsum based on the stoichiometric ratio with the KCl content, a high value of KCl conversion was achieved (95.62%).

Examination of the product from this run by X-ray powder diffraction analysis showed that a considerable amount of glaserite 3K<sub>2</sub>SO<sub>4</sub>·Na<sub>2</sub>SO<sub>4</sub> had been formed.



As far as the authors are aware, this is a completely novel route for the formation of glaserite. It is thought to be of considerable commercial potential because it would enable a highly effective recovery of the potassium content from low grade sylvinite sources (those containing high sodium content). Following a leaching step to separate any remaining gypsum, the glaserite can be further treated with sylvite or sylvinite in the presence of aqueous ammonia to yield additional K<sub>2</sub>SO<sub>4</sub>.



The K<sub>2</sub>SO<sub>4</sub> can be recovered by crystallisation (Fernandez-Lozano, 1980) with an efficiency above 99% in a state virtually free of NaCl and KCl and containing less than 1% Na<sub>2</sub>SO<sub>4</sub>.

TABLE 3  
Results Based on Solid Product Compositions at End of Runs Using KCl/NaCl Feeds

Sylvinitic Composition, wt %		Reaction Time, Min.	Solid Product, wt %			Conversions at end of reaction %		
KCl	NaCl		K <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	CaSO <sub>4</sub> ·2H <sub>2</sub> O	KCl	NaCl	CaSO <sub>4</sub> ·2H <sub>2</sub> O
71.73	28.27	90	88.10	4.09	6.71	91.69	10.37	93.25
55.80	44.20	90	87.01	7.38	4.40	86.68	8.98	95.51
39.47	60.53	100	76.77	14.97	7.45	95.62	11.76	92.82

### Comparison with Binary Solvents

Figure 7 shows experimental results that allow a comparison of the reactor performance using the newly proposed ternary mixture of hydrazine-ammonia-water with the known binary alternatives of aqueous ammonia and aqueous hydrazine. The curves show the course of the reaction between stoichiometric quantities of natural gypsum and KCl at 20°C in

1. aqueous ammonia containing 36%  $\text{NH}_3$  by weight, with a gypsum to solvent weight ratio of 1:12.
2. aqueous hydrazine containing 51.52%  $\text{N}_2\text{H}_4$  by weight, with gypsum to solvent weight ratios of both 1:12 and 1:20
3. ternary solvent containing by weight fraction 51.52%  $\text{H}_2\text{O}$ , 29.74%  $\text{N}_2\text{H}_4$  and 18.74%  $\text{NH}_3$ , with gypsum to solvent weight ratios of both 1:12 and 1:14.

While the initial rates of conversion are higher in the presence of aqueous ammonia, the yield never exceeds 87%; in fact the yield falls appreciably at high residence times, due to the conversion of  $\text{K}_2\text{SO}_4$  to syngenite. At low residence times the reaction progresses along similar lines in the presence of either aqueous hydrazine or the ternary solvent. However with hydrazine and water alone, the yield reaches a limiting value of approximately 91% with a gypsum to solvent ratio of 1 to 12. Only if the solvent charge is increased to twenty times the gypsum feed weight does the yield approach 97%. Approximately the same yield is obtained with a ternary solvent input of just twelve times the weight of gypsum. If this ratio is increased to fourteen, the  $\text{K}_2\text{SO}_4$  yield continues to rise steadily with time to a value above 99%.

A similar comparison of these solvents when processing the smaller-grained artificial gypsum would show the ter-

nary solvent in an even more favourable light. The results presented in Figure 3 indicate a 98% yield at 20°C within about 10 minutes with the ternary solvent. In a range of experiments with artificial gypsum and aqueous hydrazine no values of yield above 90% were obtained. In similar experiments with artificial gypsum and aqueous ammonia no values of yield above 90% were obtained. In similar experiments with artificial gypsum and aqueous ammonia (Fernandez-Lozano and Wint, 1982), a  $\text{K}_2\text{SO}_4$  yield above 98% occurred in just one run. However, to achieve this, this reactor had to be operated at 0°C with a solvent to gypsum ratio of 9.43.

### DISCUSSION

This paper describes a novel proposal to use a ternary liquid hydrazine-ammonia-water to promote the double decomposition of gypsum and KCl to form  $\text{K}_2\text{SO}_4$ . Certainly the results are encouraging. However, it is emphasised that the experiments form only a preliminary survey of the possible applications. A more complete experimental programme to optimise the variables affecting reactor performance could bring increased values of yield and lower residence times. For example, Figure 2 showed a simple comparison of the performances of just three different mixtures of hydrazine, ammonia and water. From these results the best of the three compositions was chosen for all later work. Clearly there is great scope for an even more effective mixture to be found within this ternary system.

The results indicate that the ternary solvent is more effective in promoting the formation of  $\text{K}_2\text{SO}_4$  than either of the previously proposed solvents, aqueous hydrazine and aqueous ammonia. In making a comparison with aqueous ammonia, it is significant that the ternary solvent generally works well at 20°C, whereas the aqueous ammonia is usually required to be cooler than this to ensure a good yield. Also the ternary solvent exerts a vapour pressure well below atmospheric pressure at 20°C, thus reducing the potential problems of vapour losses from a system being fed with solids. In making a comparison with aqueous hydrazine, it should be noted that the ternary solvent generally gives higher yields of  $\text{K}_2\text{SO}_4$  and faster rates of conversion. In addition, lower solvent-to-gypsum ratios can be used, and the presence of ammonia in the solvent will inhibit any possible decomposition of the hydrazine.

The high yields of  $\text{K}_2\text{SO}_4$  obtained in short reactor residence times from artificial gypsum, as demonstrated in Figure 3, are particularly promising for possible future commercial application. We feel that the artificial gypsum used in these tests provides a good guide for the probable behaviour of gypsum produced as a by-product from a variety of processes, such as seawater sodium chloride recovery, phosphoric acid manufacture and limestone scrubbing systems for flue gases. It should be noted that of all the results given in this paper, only two tests were with arti-

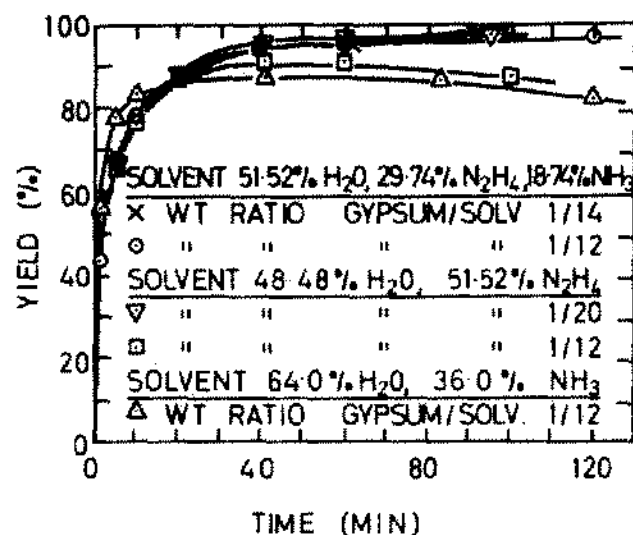


Figure 7. Comparison of the effects on the reaction of three different types of solvent.



ficial gypsum. All the other runs would probably have shown significantly higher values of yield and faster conversion rates if the natural gypsum had been replaced with artificial gypsum.

When considering the other main raw material for the process, namely KCl, the results shown in Figure 6 and Table 3 are especially encouraging. Contamination with NaCl, even to an extent where the NaCl outweighs the KCl, is no problem. The formation of glaserite  $3K_2SO_4 \cdot Na_2SO_4$  by the newly discovered reaction represented by equation (5), followed by further treatment represented by equation (6), will give a good yield of high purity  $K_2SO_4$ .

An interesting possibility for seawater sodium chloride plants concerns utilisation of the main by-product from the proposed process, namely the calcium chloride solution denoted in equation (1). This could be used for desulphation of the residual brines. It is a well-known process but generally regarded as uneconomical unless a source of low cost  $CaCl_2$  is available (D'Arcy, et al. 1967). Therefore, integration of a  $K_2SO_4$  fertiliser plant with a sodium chloride plant could be commercially attractive.

## CONCLUSIONS

The ternary solution hydrazine-ammonia-water is very effective in promoting the reaction of gypsum and potassium chloride to form  $K_2SO_4$ . It is more effective than the previously known binary solutions, namely aqueous ammonia and aqueous hydrazine. An additional advantage over aqueous ammonia is that the vapour pressure is substantially lower. The reactor can be operated at atmospheric pressure without the risk of vapour losses commonly suffered by processes requiring solid feeds.

The experimental results in a small-scale reactor have included a 99% yield of  $K_2SO_4$  from KCl when reacting with natural gypsum for 90 minutes, and a yield close to 98% when reacting with artificial gypsum for just 10 minutes. The latter result is especially interesting because the artificial gypsum probably represents the behaviour of the type of gypsum available at low cost as a by-product from a variety of processes.

Other results have shown that a high yield of  $K_2SO_4$  from KCl is obtained even when there is contamination with large amounts of NaCl. The process then operates via a previously unknown reaction route to glaserite  $3K_2SO_4 \cdot Na_2SO_4$ . This can be treated to give high purity  $K_2SO_4$  with very high recovery of the potassium content.

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