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CONVERSION OF PHOSPHOGYPSUM TO POTASSIUM SULFATE
Part I. The effect of temperature on the solubility of calcium sulfate in concentrated aqueous chloride solutions

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Solubility of calcium sulfate in concentrated aqueous chloride solutions is of particular significance in chloride hydrometallurgy and various crystallization processes, such as the production of potassium sulfate from phosphogypsum and potassium chloride. This paper examines an example of the second type of application in which gypsum and potassium chloride are reacted to form K_2SO_4. The solubility of phosphogypsum in aqueous solutions of KCl, HCl, and mixtures of both has first been measured at various temperatures and concentrations. The parameters investigated are HCl concentration up to 6M, KCl concentration up to 180 g L^{-1} and temperature from 25 to 80°C. In addition, the influence of co-existing chloride salts, such as (HCl+KCl), on the solubility of calcium sulfate is estimated from 25 to 80°C. The solubility increases obviously with the temperature increment as it does initially with acid concentration, reaching a maximum of about 3M HCl, 130 g L^{-1} KCl and then drops. At the same time, the solubility of $CaSO_4{\cdot}2H_2O$ decreases with increasing KCl concentration.

Keywords: *calcium sulfate, conversion, hydrochloric acid, potassium chloride, potassium sulfate, solubility*

Introduction

Phosphogypsum tailings are solid mineral wastes of the production of phosphoric acid from phosphate rock. For every ton of phosphoric acid produced, about 5 tons of phosphogypsum are generated, depending on the quality of the phosphate ore:

$$3H_2SO_4(l)+Ca_3(PO_4)_2(s)+6H_2O(l)\rightarrow$$
$$\rightarrow 2H_3PO_4(l)+3CaSO_4{\cdot}2H_2O(s)$$

More than 22 million tons of phosphoric acid are produced annually worldwide, generating in excess of 110 million tons of phosphogypsum by-products. Depending on the reaction temperature used to produce phosphoric acid, either the dehydrate ($CaSO_4{\cdot}2H_2O$) or the hemihydrate ($CaSO_4{\cdot}1/2H_2O$) form is generated as a by-product filter cake. The free water in the gypsum cake is about 25% and is highly acidic, having a lower pH.

The problem of the elimination of phosphogypsum as a waste will be assessed in greater detail below but the possibilities of making use of phosphogypsum are of interest when its quality is improved amongst other means in order to be recuperated to the processes which involve putting the calcium sulfate through various crystalline phases in order to purify it. Then it is no longer a waste but a by-product of preparation of phosphoric acid which could replace natural gypsum for most of the applications of the latter, such as in the manufacture of plaster and cement industry.

Plaster and cement industry

The crystallization of gypsum ($CaSO_4{\cdot}2H_2O$) from a suspension of calcium sulfate hemihydrate is well-known as the setting of plaster. Badens *et al.* [1–2] present results concerning the crystallization of gypsum in the presence of different carboxylic acids. The influences of additives on the crystallization kinetics and on the morphology of gypsum crystal have been studied. The rate retarding effect was determined by recording the conductivity of suspension of hemihydrate *vs*. time.

The setting of gypsum plaster in the presence of cellulose ether (CE) was studied by monitoring the kinetics of bassanite (calcium sulfatehemihydrate, HH) dissolution and of gypsum (calcium sulfate dehydrate, DH) precipitation [3]. The presence of CE under industrially relevant conditions of 0.25 mass% retards the dissolution rate by 50%. The incubation time for DH nucleation is extended by 100% in the presence of 0.25 mass% CE. It concludes that the interaction between CE and HH as well as DH surfaces is weak and the dissolution and precipitation processes are affected primarily due to the diffusion properties of dissolved Ca^{2+} and SO_4^{2-} species in CE solution.

Set plaster is obtained from the dehydration of natural gypsum ($CaSO_4{\cdot}2H_2O$) into calcium sulfate hemihydrate ($CaSO_4{\cdot}0.5H_2O$) and anhydrites (γ-$CaSO_4$ and β-$CaSO_4$) [4]. The dehydration was carried out by heating under a constant pressure of water vapor using controlled transformation rate thermal analysis.

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In South Africa, major gypsum deposits are located far from the cement-producing plant. Increasing transport costs have forced cement companies to consider seriously the replacement of natural gypsum by phosphogypsum resources. An investigation was therefore carried out to determine the effect of various treatments of phosphogypsum on the performance of cement made with it. The investigation focused specially on setting times and strength development of cement containing phosphogypsum instead of natural gypsum [5].

In the construction industry, a study based on the results of an experimental investigation on Fly ash–lime–phosphogypsum hollow blocks is presented [6]. The compression strength, water absorption and mass of FaL-G hollow blocks were determined. The durability of these blocks in terms of loss in compression strength in sulfate environments is also presented in this paper. It is observed that FaL-G hollow blocks have sufficient strength for their use in general building construction.

Phosphogypsum PG can be stabilized with class C fly ash and lime for potential use in marine environments [7]. An augmented simplex centroid design with pseudo-components was used to select 10 PG:class C fly ash:lime compositions. When the PG:class C fly ash:lime composites were submerged, saltwater was able to intrude throughout the entire composite and dissolve PG. The dissolution of PG increased the concentration of sulfate ions that could react with calcium aluminum oxides in class C fly ash forming additional ettringite that accelerated rupture development. Development of ruptures in the composites must be considered when the composites are used for aquatic applications.

Ammonium and potassium sulfate

In the α hemihydrate or dehydrate state, it is used aiming to recover the SO_4 content in manufacturing of ammonium or potassium sulfate by the double decomposition reaction.

Ammonium sulfate for use as fertilizer, supplying sulphur as well as nitrogen to soils, can be manufactured from anhydrous ammonium carbonate and gypsum or anhydrite. Elkanzi studied the kinetics of the conversion of calcium sulfate to ammonium sulfate using ammonium carbonate aqueous solution [8]:

$$CaSO_4{\cdot}2H_2O+(NH_4)_2CO_3\rightarrow$$
$$\rightarrow CaCO_3+(NH_4)_2SO_4+2H_2O$$

Bani-Kananeh *et al.* present results concerning the production of potassium sulfate by the double decomposition reaction of potassium chloride and phosphogypsum in aqueous ammonia solution at low temperatures [9]:

$$CaSO_4{\cdot}2H_2O+2KCl\rightarrow K_2SO_4+CaCl_2{\cdot}2H_2O$$

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 Lozano studied the kinetics of the reaction of the production of glaserite and potassium sulfate from gypsum and sylvinite catalyzed by ammonia [10, 11].

Balarew studied the conversion of $CaSO_4$ to $CaCO_3$ within the $CaSO_4+Na_2CO_3\leftrightarrow CaCO_3+Na_2SO_4$ four-component water-salt system [12]. A 98% degree of conversion was achieved by using $CaSO_4{\cdot}2H_2O$ isolated from waste brine in the production of sea salt.

Soil amendment

Furthermore, it was shown that the addition of phosphogypsum to certain consolidating soils strongly improved permeability and water uptake [13].

Calcium deficiency and aluminum toxicity are among the main factors limiting the productivity of crops cultivated on acidic soils, which are predominant in Brazil. Therefore, phosphogypsum can be considered a good amendment for subsoil that presents toxic levels of aluminum and/or calcium deficiency [14].

In Carvalho's research, the effect of calcium sulfate, phosphogypsum and calcium carbonate on chemical soil properties and soil solution composition for subsoil samples from five acid soils was compared and an evaluation was made on how these changes in soil properties affected root development and water and nutrient uptake by maize grown in the greenhouse [14].

Previous solubility studies

Some earlier experimental data on the solubility of calcium sulfate in some chloride aqueous solutions were reported in two main handbooks [15, 16]. The solubility of calcium sulfate in chloride aqueous solutions has been studied by several investigators, but mainly the studies dealt with the behavior of gypsum (calcium sulfate dehydrate) at low temperature.

The solubility of gypsum in organic acids namely acetic, oxalic, tartaric and succinic acids at low temperature (30°C) was studied [17]. The results show that sulfate sulphur content increases with increasing acid concentration from 0.1 to 0.25M and decreases again at higher concentration. The solubility of gypsum in 0–30 mass% nitric acid solutions at 20°C was also studied [18].

The solubility of calcium sulfate dehydrate in HCl-$CaCl_2$ solutions was determined by Li and Demopoulos [19]. The parameters investigated are HCl concentration up to 5M, $CaCl_2$ concentration up to 2M and temperature from 20 to 80°C.

Solubility of calcium sulfate in concentrated aqueous chloride solutions are of particular significance in chloride hydrometallurgy and various crystallization processes, such as the production of potassium sulfate from phosphogypsum and potassium chloride. This paper examines the solubility of $CaSO_4{\cdot}2H_2O$ in aqueous solutions of KCl, HCl, and mixtures of both measured first at various temperatures and concentrations. Understanding the dissolution behavior of $CaSO_4{\cdot}2H_2O$ is of major interest for designing many environmental processes, as for example the second type of application in which gypsum and potassium chloride are reacted to form K_2SO_4.

Experimental

The calcium sulfate dehydrate used in this research was from reagent grade chemicals, with the purity of 99%. The potassium chloride salt was Fisher certified reagents of high purity. The experiments were done using a 1-L reaction vessel which was heated to ±0.1°C in temperature-controlled circulating water bath. Excess amount of calcium sulfate dehydrate was dissolved in HCl, KCl and their mixed aqueous solutions of required concentration and was kept stirring magnetically for 5 h. This was determined to be adequate for reaching equilibrium. The solubility of gypsum in these solutions is determined as the difference in gypsum mass before and after dissolution divided by the total volume of the solution mixture.

Solubility of $CaSO_4{\cdot}2H_2O$ in HCl solution

Calcium sulfate dehydrate solubility at room temperature in hydrochloric acid solution with the concentration of up to 6M HCl is tabulated in Table 1 and shown in Fig. 1 with other experimental data at higher temperature (80°C).

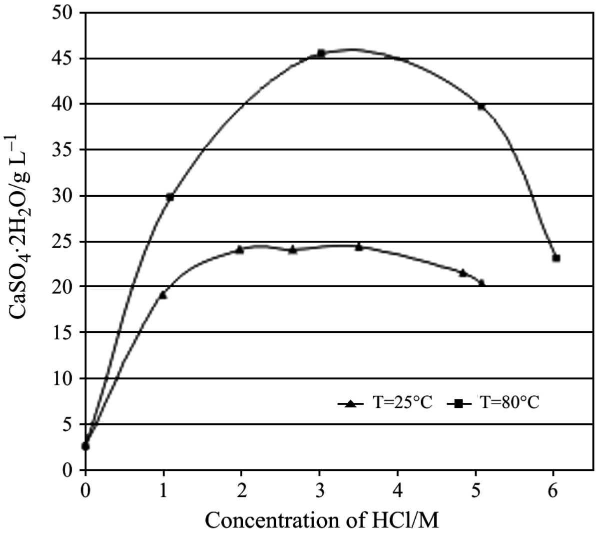

Fig. 1 Solubility of $CaSO_4{\cdot}2H_2O$ in HCl solution at 25 and 80°C

Here the solubility of $CaSO_4{\cdot}2H_2O$ is sharply increased as the concentration of HCl is increased (Fig. 1). This increase in solubility might be due to the affinity of HCl to dissolve (and react with) gypsum leaving it in ionic form. This affinity also increases with the increase in solution temperature, where the solubility in the 3M HCl solution reached 47 g L^{-1} at 80°C compared to 24 g L^{-1} at 25°C. It is also seen that the solubility of calcium sulfate increases with the

Table 1 Solubility of $CaSO_4{\cdot}2H_2O$ in aqueous chloride solutions

Concentration	$CaSO_4{\cdot}2H_2O$ solubility/g L^{-1}	
	T=25°C	*T*=80°C
KCl concentration/g L^{-1}		
0	2.7818	
20.0028	4.9456	
40	6.4844	
60	7.4156	
80	8.4956	
100	8.7532	
130	8.7144	
140	4.484	
160	3.718	
0		2.4712
20		5.121
40		6.191
60.007		7.288
80.007		7.944
100		8.312
140		9.005
180		6.658
HCl concentration/mol L^{-1}		
0	2.7818	
0.9888	19.14	
1.9771	24.052	
2.6574	24.058	
3.50305	24.4	
4.8318	21.513	
5.0733	20.301	
0		2.4712
1.0875		29.8
3.0198		45.476
5.0734		39.666
6.0388		23.086
(HCl+KCl) concentration/g L^{-1}		
0	2.7818	
20	14.859	
60	25.318	
100	28.622	
120	16.319	
0		2.47
20		20.901
60		44.975
100		41.587
120		53.542
140		45.092

temperature. However, the solubility of $CaSO_4$ at 80°C decreases dramatically with the HCl concentration higher than 3M.

Solubility of $CaSO_4·2H_2O$ in KCl solution

As shown in Fig. 2, the solubility of $CaSO_4·2H_2O$ is slightly increased with the increase the concentration of KCl (compared with the HCl concentration). This might be due to the reaction between KCl and $CaSO_4·2H_2O$, but, at higher KCl concentrations, the tendency the double salt formation increases.

While the KCl concentration is less than 130 g L^{-1}, the effect of the temperature on the solubility of the gypsum is negligible. On the other hand, the solubility of $CaSO_4·2H_2O$ at 25°C decreases dramatically when the KCl concentration is more than 130 g L^{-1}.

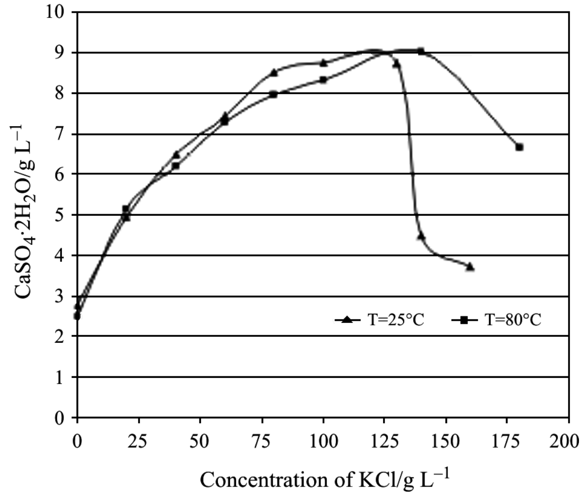

Fig. 2 Solubility of $CaSO_4·2H_2O$ in KCl solution at 25 and 80°C

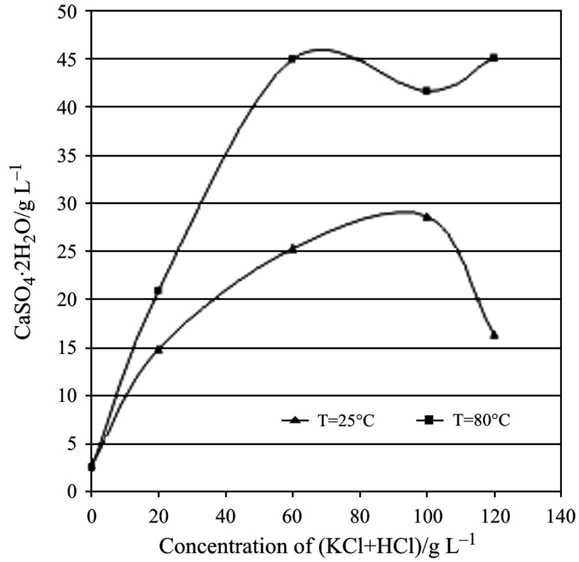

Fig. 3 Solubility of $CaSO_4·2H_2O$ in (HCl+KCl) solution at 25 and 80°C

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

Figure 3 shows that the solubility of the $CaSO_4·2H_2O$ in 1:1 KCl to HCl solution increases with the increase in the concentration of the KCl+HCl mixture and temperature. This solubility is near to the solubility of gypsum in HCl solution alone (Figs 4 and 5).

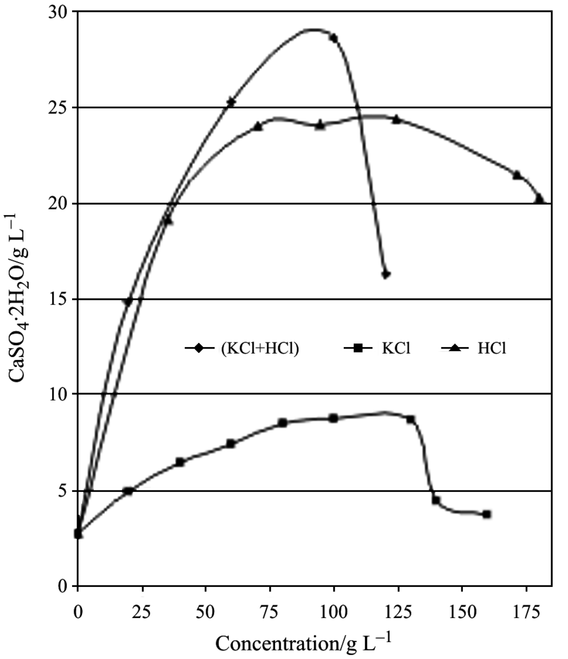

Fig. 4 Solubility of $CaSO_4·2H_2O$ in HCl, KCl and (HCl+KCl) solution at 25°C

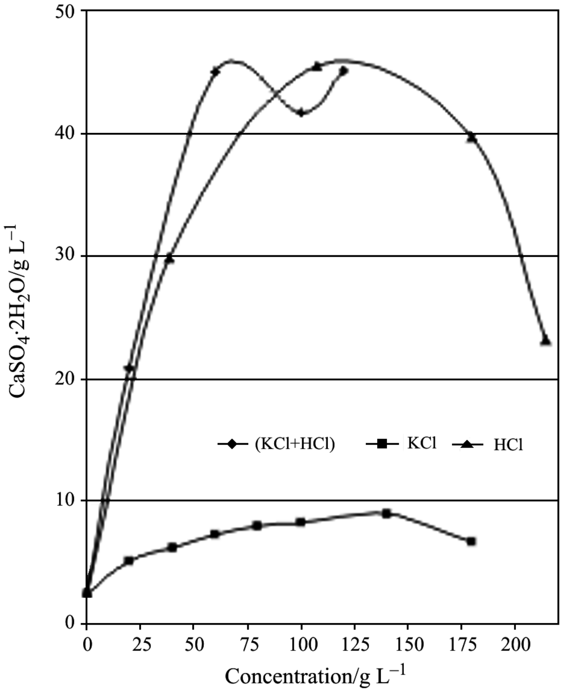

Fig. 5 Solubility of $CaSO_4·2H_2O$ in HCl, KCl and (HCl+KCl) solution at 80°C

Finally, it is clear that gypsum has its highest solubility in the HCl solution and its lowest solubility in the KCl solution. It reaches 25 g L^{-1} at 25°C in 3M HCl solution compared to 30 g L^{-1} for a 1:1 KCl to HCl solution and 9 g L^{-1} for KCl solution.

In the 1:1 KCl to HCl solution, the presence of HCl increases the solubility of gypsum and decreases the tendency for the double salt formation, while the presence of KCl oppositely increases the tendency to the double salt formation.

Production of potassium sulfate:

Firstly, the conversion of $CaSO_4 \cdot 2H_2O$ to K_2SO_4 has been studied in the absence of ammonia solution and alcohol at 25°C. As shown in Fig. 6, the maximum conversion of $CaSO_4 \cdot 2H_2O$ achieved was about:

- 40% for stoichiometric reaction in 7 min
- 68% for 50% excess of $CaSO_4 \cdot 2H_2O$ in 18 min
- 87% for 100% excess of $CaSO_4 \cdot 2H_2O$ in 55 min

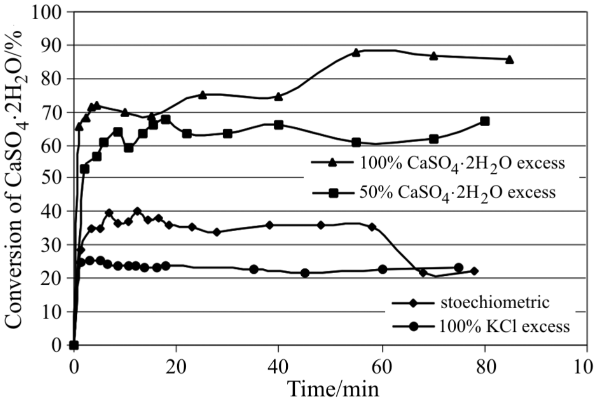

Fig. 6 Conversion of $CaSO_4 \cdot 2H_2O$ to K_2SO_4 at T=25°C

On the other hand, the maximum of $CaSO_4 \cdot 2H_2O$ conversion to K_2SO_4 was only about 35% in 3 min for 100% excess of KCl in 3 min.

Conclusions

While the KCl concentration is less than 130 g L^{-1}, the effect of temperature on the solubility the gypsum is negligible. On the other hand, the maximum of the solubility of $CaSO_4 \cdot 2H_2O$ at 25°C is only 9 g L^{-1}. The solubility decreases dramatically when the concentration of KCl is more than 130 g L^{-1}.

The maximum of the solubility of $CaSO_4 \cdot 2H_2O$ is in the 3M HCl solution. It reached 47 g L^{-1} at 80°C compared to 24 g L^{-1} at 25°C. The solubility of the $CaSO_4 \cdot 2H_2O$ in (KCl+HCl) solution is near to the solubility of gypsum in HCl solution alone. The maximum of $CaSO_4 \cdot 2H_2O$ conversion to K_2SO_4 at T=25°C is about 87 for 100% excess of $CaSO_4 \cdot 2H_2O$ in 55 min.

Future work needs to be done to optimize the conversion of $CaSO_4 \cdot 2H_2O$ to K_2SO_4 in the presence of ammonia solution and selected alcohol at 25°C.

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