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Study of the Sylvite Transformation into Arcanite At 25°C

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Abstract: It is known that arcanite (K_2SO_4) can be manufactured, by a double decomposition reaction, from sylvite (KCl) and a sulphate component namely the magnesium sulphate. For this latter salt, the considered transformation can be done in one or two stages indicated respectively by mode «A» and mode «B». Theoretical yield calculations allowed us to choose the mode «B» to be experimentally studied. A systematic study of the transformation, using conductimetric measurements, showed that two hours reaction time is sufficient to obtain a potassium sulphate whose quality becomes commercial with a simple washing.

Key words: Reciprocal quaternary system . Transformation . Sylvite . Epsomite . Arcanite

INTRODUCTION

Potassium sulphate is mainly used as an agricultural fertilizer because it is a source of soluble potassium, an important nutrient for the plants' growth [1]. This mineral, especially recommended for crops sensitive to chloride, is rarely found in nature and, in many cases, has to be produced by chemical reactions. It is generally manufactured from sylvite (KCl) and a sulphate component [2, 3].

In the present work, potassium chloride and magnesium sulphate are the reagents used for potassium sulphate production. They are converted by double decomposition in a single or multistage process according to the reaction:

$$2KCl + MgSO_4 \leftrightarrows K_2SO_4 + MgCl_2$$

The reagents may be recovered from Tunisian natural brines, which are estimated to be about 6.10^6 m^3 with a salinity average of 300 $g.L^{-1}$ [4]. Generally, conventional procedures, like crystallization under natural conditions, [5, 6] are used to extract the above reagents.

The aim of this study is to determine time reaction of the sylvite (KCl) and epsomite ($MgSO_4.7H_2O$) transformation into arcanite (K_2SO_4) using conductimetric measurements.

DESCRIPTION OF THE TRANSFORMATION

The studied transformation obeys the above mentioned reaction. It is an application of the reciprocal quaternary diagram: K_2Cl_2, $MgCl_2$, K_2SO_4, $MgSO_4$ // H_2O (K_2Cl_2 is not dimmer specie; it is introduced to get the same charges number for all ions.).

Considering Fig. 1, which represents the 25°C isotherm of this diagram [7], this transformation can be done in one or two stages indicated respectively mode "A" and mode "B".

For the first mode, the raw materials are epsomite ($MgSO_4.7H_2O$), sylvite (KCl) and water. The reaction products are arcanite (K_2SO_4) and a saturated aqueous solution having the composition of point "R" (Fig. 1). The corresponding reaction is the following:

$$MgSO_4.7H_2O_{(sd)} + 2KCl_{(sd)} + H_2O \leftrightarrows K_2SO_{4(sd)} + \text{"R" solution} \quad (1)$$

The second mode is a two stages procedure. In the first stage, sylvite and epsomite are mixed with water in the proportion of point m' (Fig. 1). The products of this reaction are schoenite ($K_2SO_4.MgSO_4.7H_2O$) and a saturated aqueous solution having the composition of point "D" (Fig. 1). Schoenite which is an intermediate product was separated from mother liquor by filtration. In the second stage, schoenite provided from the first

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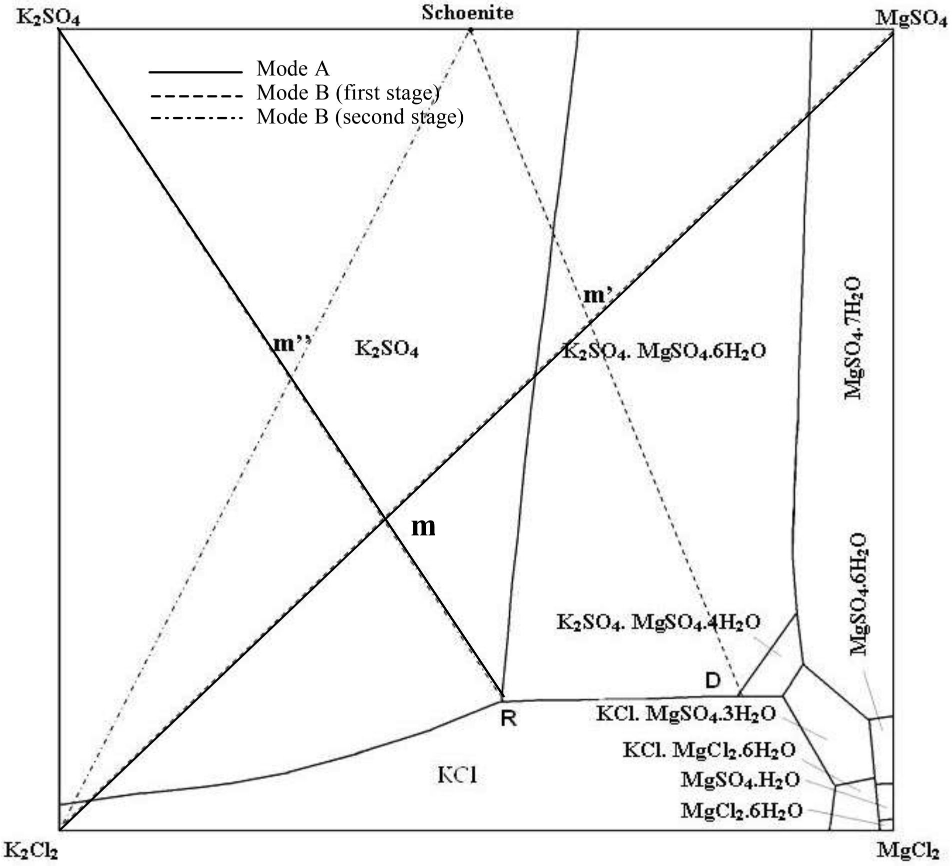

Fig. 1: Jänecké projection of the reciprocal quaternary system K^+, Mg^{2+} / Cl^-, SO_4^{2-}// H_2O at 25°C

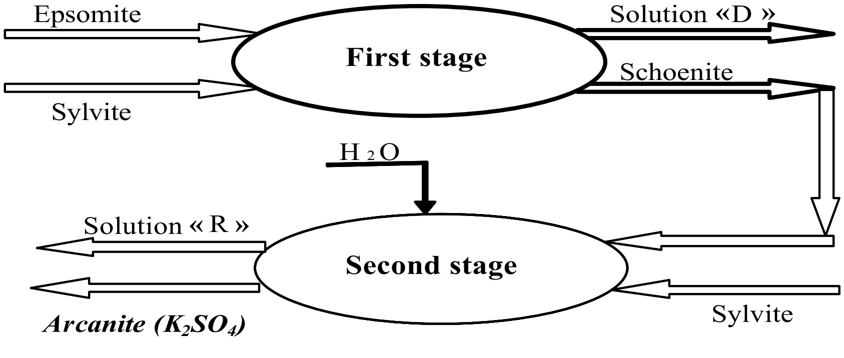

Fig. 2: Transformation diagram according to the mode B

stage is mixed with water and sylvite, in the proportion of point m", to give arcanite (K_2SO_4) and a saturated solution whose composition is equivalent to that of point "R".

The corresponding reactions are written as below:

- First stage:

$$MgSO_4.7H_2O_{(sd)} + 2KCl_{(sd)} + H_2O \leftrightarrows K_2SO_4.MgSO_4.6H_2O_{(sd)} + \text{"D" solution} \quad (2)$$

- Second stage:

$$K_2SO_4.MgSO_4.6H_2O_{(sd)} + 2KCl_{(sd)} + H_2O \leftrightarrows K_2SO_{4(sd)} + \text{"R" solution} \quad (3)$$

Theoretical yield calculations (Table 1) allowed us to choose the mode B to be experimentally studied for; the sulphate total output of the two stages process (73.84%) is higher than that of the transformation performed according to the mode A (67.85%) [8, 9].

Table 1: Theoretical yields in sulphate and potassium ions for the mode A and the mode B

		Mode B	
	Mode A	1st stage	2nd stage
The yield in sulphate ions	67.84	87.98	83.92
The yield in potassium ions	45.75	84.97	67.60
The global yield in sulphate ions	67.84	73.84	
The global yield in potassium ions	45.75	63.10	

Figure 2 shows the transformation diagram according to the mode B.

EXPERIMENTAL DETAILS

Chemicals: All the reagents used were of analytical grade, except the double salt “schoenite ($K_2SO_4.MgSO_4.6H_2O$)”, which was obtained experimentally as a product of the first stage. The sylvite (99%) and epsomite (99.9%) were supplied by FLUKA. All the aqueous solutions were prepared in distilled water.

Apparatus and analysis methods: The obtained liquid phases were chemically analyzed. The K^+ ion concentrations in the phases were analyzed by spectrophotometer using a Jenway PFP7 instrument. The Mg^{2+} ion concentrations were determined by an EDTA complexometric titration. Potentiometric titration was applied to Cl^-ions (Titrino DMS 716, O Metrohm instrument). The SO_4^{2-}ion concentrations were determined gravimetrically. The solid phases were often characterized by chemical analysis and XRD (the experimental apparatus is composed of a Philips PW 1730/10 generator, a PW 1050/81 goniometer and a PW 2233/20 copper cathode). The conductivity measurement was performed by using a Consort conductimeter (Consort C 832 provided with a conductimetric cell Consort K = 9.76 cm^{-1}, specific to high concentrated solution).

Procedures and equipments: The two stages of the double decomposition reaction were carried out successively in a batch way at 25°C, in a thermostatic cell. The temperature was controlled by circulating water in the jacket, by means of a thermostatic bath. The mixture was continuously agitated by a mechanic stirrer. The formed suspension conductivity as a function of time was measured when the totality of the three reagents was introduced in the thermostatic cell.

To study the influence of procedure on the product quality, the first stage mixture point (m’) was prepared according to three different methods (M1, M2 and M3). They are defined as below:

Table 2: R, D, m’ and m” Jänecké coordinates at 25°C

Coordinates	R	D	m'	m"
X_{Mg}	55.42	87.8	65.8	28.6
Y_{SO4}	17.82	18.83	65.8	57.6
Z_H	888	663	366	456

Table 3: Chemicals proportions used to perform the first and the second stage at 25°C

1st stage			2nd stage		
$m_{sylvite}$ (g)	$m_{epsomite}$ (g)	m_{water} (g)	$m_{sylvite}$ (g)	$m_{schoenite}$ (g)	m_{water} (g)
96.82	307.62	92.7	94.39	189.43	197.9

M1: Progressive addition of dry potassium chloride to a previously prepared epsomite solution.

M2: Epsomite and potassium chloride were mixed together to obtain a homogeneous solid mixture before the addition of water. This method allowed to work at constant Jänecké coordinates [10] of the mixture point (on the reciprocal quaternary system K^+, Mg^{2+} / Cl^-, SO_4^{2-}// H_2O: m’, for the first stage and m” for the second one). Only the Z_H coordinate decreases until reaching the m’ or m” point respectively for stage 1 or 2.

M3: Progressive addition of a previously prepared epsomite solution to a determined amount of potassium chloride.

The second stage mixture point (m”) was prepared according to the method, which gives the best result for first stage.

Reagents amounts determination: To prepare mixtures corresponding to the point m’ and m” (Fig. 1), the Jänecké coordinates of point “R” and “D” at 25°C [7, 8] were relieved from literature. However, the Jänecké coordinates of point m’ and m”, gathered in Table 2, were graphically determined.

The proportions of the reagents (Table 3) used to produce the schoenite at the first stage and arcanite at the second one were calculated by using the following equations:

- First stage:

$$m_{KCl} = P'(1-0.01X'_{Mg})\times M_{KCl}$$

$$m_{MgSO_4.7H_2O} = \frac{P'Y'_{SO_4}}{200}\times M_{MgSO_4.7H_2O}$$

$$m_{H_2O} = 250-(7\times 18\frac{P'X'_{Mg}}{200})$$

where,

$P' = \frac{100 \times (250/18)}{Z'_H}$, X'_{Mg}, Y'_{SO_4} and Z'_H are the Jänecké coordinates of m'.

- Second stage:

$$m_{schoenite} = \frac{P'' Y''_{SO_4}}{200} \times \frac{M_{SO_4}}{w_{SO_4}}$$

$$m_{KCl} = \left[P''\left(1 - 0.01X''_{Mg}\right) - \frac{w_K \times m_{schoenite}}{M_K} \right] \times M_{KCl}$$

$$m_{H_2O} = 250 - w_{H_2O} \times m_{schoenite}$$

where, $P'' = \frac{100 \times (250/18)}{Z''_H}$, X''_{Mg}, Y''_{SO_4} and Z''_H are the Jänecké coordinates of m".

$w_{SO_4}(44.5\%)$, $w_K(18.77\%)$ and $w_{H_2O}(27.52\%)$ are the mass percent of SO_4, K and water in the schoenite used for the second stage.

RESULTS AND DISCUSSION

First stage: Liquid and solid phases formed by first stage of the double decomposition reaction, were noticed (F1, S1), (F2, S2) and (F3, S3) respectively for the methods M1, M2 and M3. These phases were physicochemically characterized. Moreover, the solid phases were characterised by XRD (Fig. 3). As it was expected the solid phase is mainly consisted of schoenite.

Table 4 gives the chemical analysis of these six phases. It is shown that the composition of solid and liquid are those predicted by the 25°C isotherm of the quaternary reciprocal system K^+, Mg^{2+} / Cl^-, SO_4^{2-}// H_2O. From these analytical results, the Jänecké coordinates were calculated for each filtrate and each salt. The obtained results are gathered in Table 5. Jänecké coordinates values of the experimental and the theoretical points are similar.

All the experimental phases were represented in Fig. 4. As can be seen, the intermediary products move away gradually from the theoretical schoenite (Sc) in the order S2, S3, S1. Also, it can be noticed that the F3 filtrate is the nearest to the theoretical point "D" followed by F1 then F2.

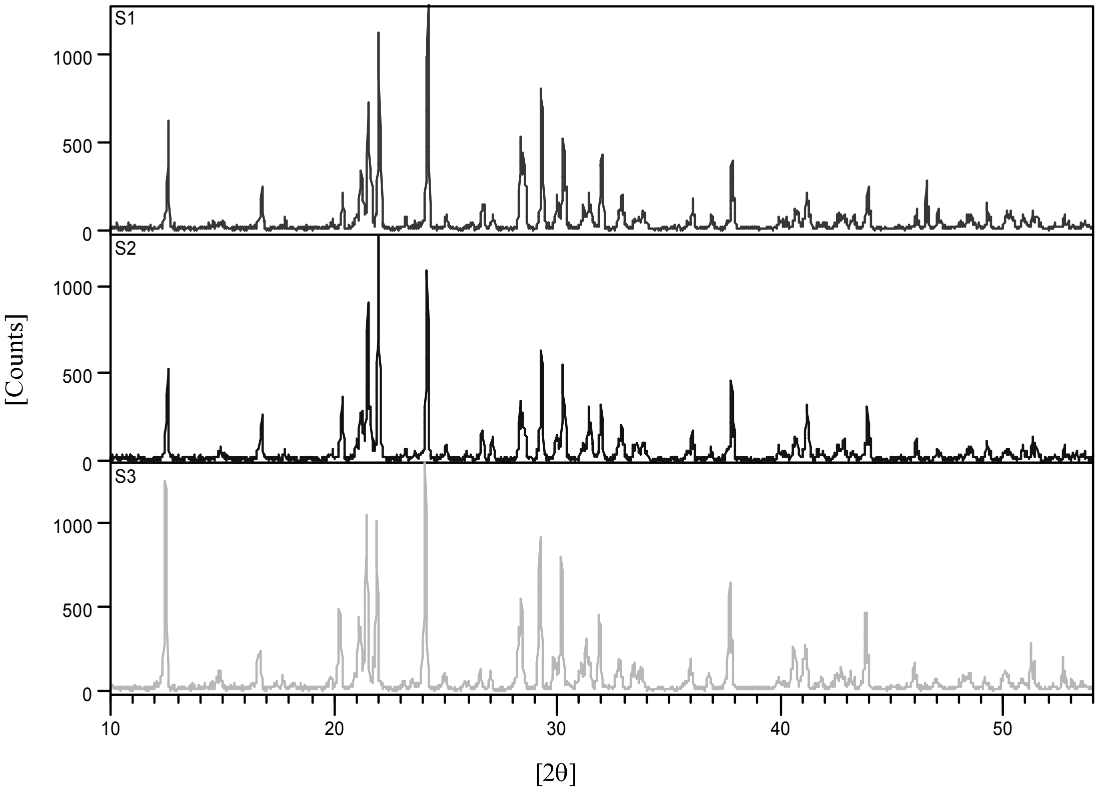

Fig. 3: XRD of the first stage products synthesized according to the methods M1, M2 and M3

Table 4: Filtrates and solids chemical analysis (first stage)

	Filtrates (g L^{-1})			Salts (%)		
	F1	F2	F3	S1	S2	S3
K^+	37.23	37.77	38.76	21.39	18.77	17.66
Mg^{2+}	69.86	63.79	70.11	5.85	5.66	5.87
Cl^-	178.80	163.50	170.10	6.46	3.55	3.78
SO_4^{2-}	74.51	77.28	69.15	44.53	44.50	41.76

Table 5: Filtrates and salts Jänecké coordinates (First stage)

	Filtrates				Salts			
	D_{theo}	F1	F2	F3	Schoenite	S1	S2	S3
X_{Mg}	87.80	85.79	84.45	85.33	50	46.84	49.26	51.69
Y_{SO4}	18.83	23.14	25.88	21.29	100	90.11	97.95	93.40

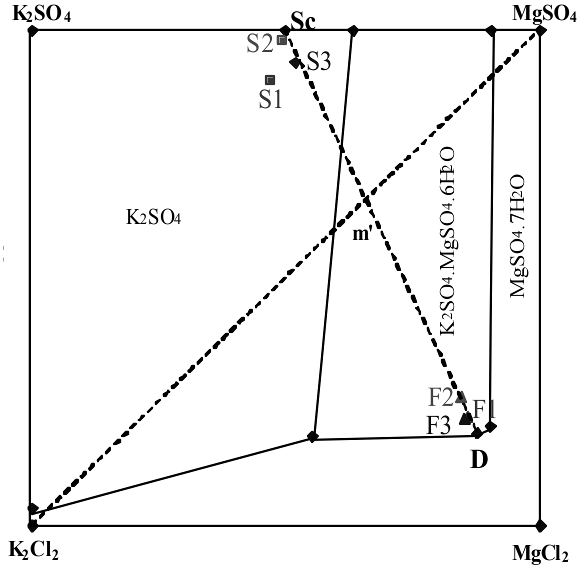

Fig. 4: Positions of the experimental points on the reciprocal quaternary diagram K^+, Mg^{2+}/Cl^-, SO_4^{2-}// H_2O at 25°C

Considering these observations particularly solid S2 physico chemical characteristics, it was reasonable to use the second method (M2) to continue this investigation.

We propose hereafter to pursue the evolution of the transformation as a function of time. For this purpose the parameter conductance of the aqueous phase was chosen as an indicator of the reaction evolution since it is directly related to the concentration of the ionic species which are present. Moreover, the end of the reaction can be recognized when the aqueous phase conductance becomes constant.

The aqueous phase samples were withdrawn at regular time intervals for conductimetric analysis then reintroduced in the jacketed glass reactor. The experimental results obtained for the first stage performed according to the method M2 are represented in Fig. 5. This figure shows the succession of three steps during the schoenite formation process. The first one corresponds to the interval [0-8 min] and could explain the dissolution of the reagents sylvite and epsomite. The segment [AB] which represents this step has a high slope which seems to indicate fast kinetics dissolution of the previously mentioned reagents. Beyond the point B the slope decreases, a second segment [BC] is recorded. This signals the appearance of a new phase in the interval [8-28 min]. At the end of this step the conductance becomes constant, which indicates the chemical equilibrium establishment and consequently the end of the reaction. Thus we can conclude that a 30 minutes reaction time is sufficient to carry out the first stage (synthesis of the schoenite from sylvite and epsomite) of the studied transformation.

Second stage: To carry out this stage, the experimentally obtained schoenite S2 was used. The corresponding mixture was prepared according to the method M2 and the quantities of reagents are those given in Table 3.

Characterization of the formed phases: The obtained solid and liquid phases were respectively noted P2 and R2. The chemical analyses results of these two phases are gathered in Table 6 and their Jäneckée coordinates are indexed in Table 7.

These two tables show that the composition and the Jänecké coordinates of the liquid phase R2 are comparable to those of the invariant point R, which represents the solution R (a liquid phase in equilibrium simultaneously with three salts (schoenite, sylvite and arcanite)). For the wet solid phase P2, it contains exogenic ions and the values of its Jänecké co-ordinates are different from those of the theoretical point.

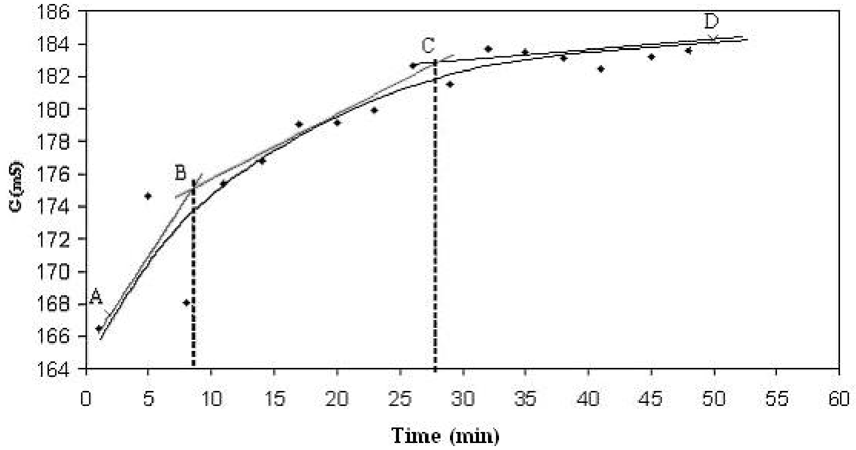

Fig. 5: Variation of the aqueous phase conductance as function of time (first stage, method M2) at 25°C

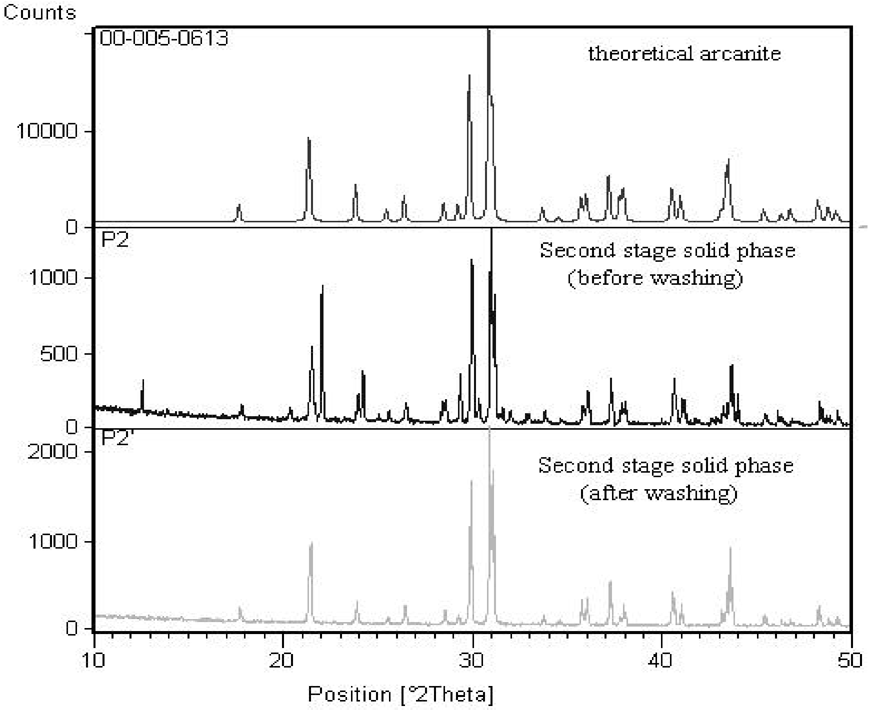

Fig. 6: Second stage solid phase XR diffractograms (before and after purification)

This result is confirmed by XRD (Fig. 6), showing that the solid phase obtained (P2) corresponds to potassium sulphate containing impurities. These latter come from crystals coating solution and probably from a small proportion of salts which can co-precipitate with K_2SO_4.

Purification of formed salt: To improve the chemical quality of the end product obtained, we tried to purify it by a washing with a potassium sulphate saturated solution. The chemical analysis results (Table 6) and

Table 6: Chemical analysis for the filtrate R2 and solids P2 and P2' (second stage)

	Filtrate (g L^{-1})	Salts (%)	
	R2	P2	P2'
K^+	66.83	36.26	36.49
Mg^{2+}	41.07	1.95	0.46
Cl^-	155.6	4.37	0.74
SO_4^{2-}	46.98	43.06	46.65

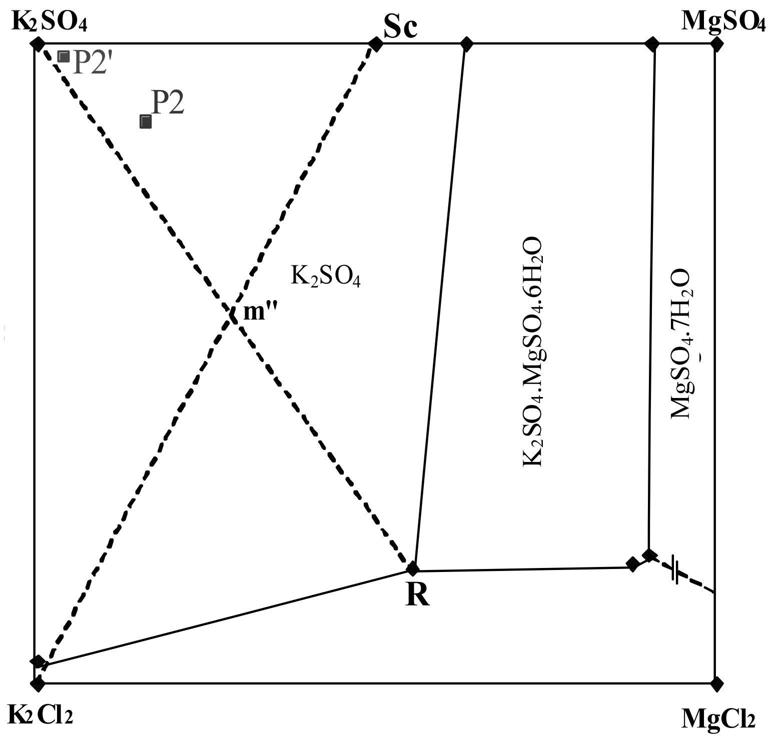

Fig. 7: Positions of the solid phase P2, before and after purification, on the reciprocal quaternary diagram K^+, Mg^{2+} / Cl^-, SO_4^{2-}// H_2O at 25°C

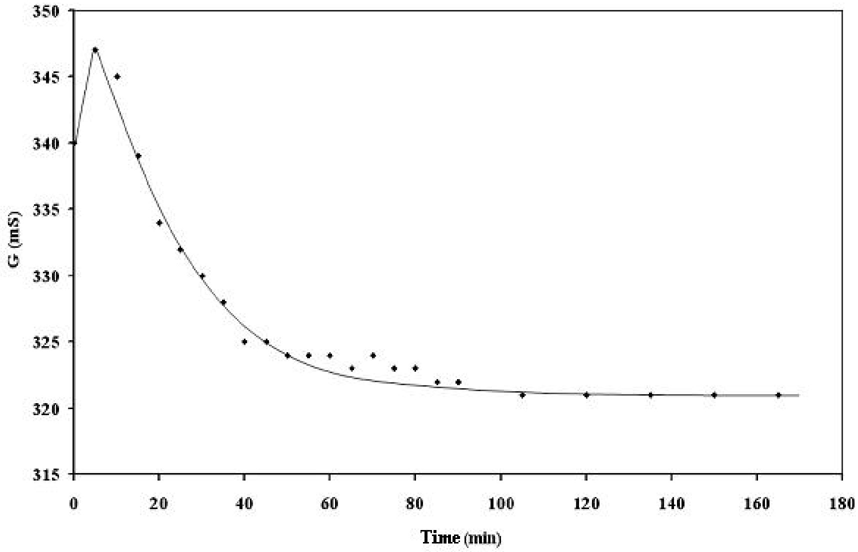

Fig. 8: The aqueous phase conductance variation as function of time (Second stage, method M2) at 25°C

the Jänecké coordinates values (Table 7) of the after washing product (noted P2') show that it is constituted of more than 98% of arcanite (K_2SO_4). The x-ray diffractogram of this solid phase and its position on the reciprocal quaternary diagram are respectively represented in Fig. 6 and 7.

Table 7: Jänecké coordinates of the filtrate R2 and the salts P2 and P2' (second stage)

	Filtrates		Salts		
	R_{theo}	R2	Arcanite	P2	P2'
X_{Mg}	55.42	62.95	0	15.74	3.83
Y_{SO4}	17.82	18.23	100	87.92	97.87

Reaction time determination: As the first stage, the aqueous phase conductance was followed as function of time in order to estimate the second stage time reaction. The obtained results were represented in Fig. 8.

This figure shows that the aqueous phase conductance increases until reaching a maximum value which indicates the aqueous solution saturation. At this moment, potassium sulphate precipitation starts and the aqueous phase conductance decreases until reaching a constant value which indicates the chemical equilibrium establishment and consequently the end of the reaction.

Also, it can be noticed that the aqueous phase conductance becomes constant after 90 minutes which is the needed time to carry out the second stage of the double decomposition reaction.

Considering the necessary time to perform the first stage it can be concluded that two hours are sufficient to prepare the potassium sulphate according to the considered transformation.

CONCLUSION

The potassium sulphate synthesis from sylvite (KCl) and epsomite ($MgSO_4.7H_2O$) can be done in one or two stages. The study presented in this paper is a contribution to a better understanding of the two stages procedure and also to determine the reaction time for each of the two stages of the considered double decomposition reaction at 25°C.

It was shown that a reaction time of two hours is necessary for this two stages transformation and the corresponding process must include a washing operation after which the ultimate product becomes commercial. Finally it should be noticed that the chemical equilibrium is more quickly reached for the first stage of the studied transformation.

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