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**EXPERIMENTAL PRODUCTION OF KCl AND MgO  
UTILIZING CARNALLITE AS RAW MATERIAL**  
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## RESUME

*Les réserves de carnallite (KCl.MgCl<sub>2</sub>.6H<sub>2</sub>O) au Brésil sont évaluées à 24 milliards de tonnes de minerai « in situ ». Elles ne sont pas exploitées en raison de l'absence de procédé industriel applicable économiquement dans les conditions locales.*

*Dans cette étude, un procédé de récupération du potassium et du magnésium de la carnallite est proposé. Dans un premier stade du procédé, une solution aqueuse de carnallite est ammoniée pour favoriser la précipitation de KCl, NH<sub>4</sub>Cl and Mg(OH)<sub>2</sub>. Après séparation de la liqueur mère, KCl et NH<sub>4</sub>Cl sont redissous dans l'eau ce qui permet la séparation de Mg(OH)<sub>2</sub> par centrifugation. Ensuite, KCl et NH<sub>4</sub>Cl peuvent servir de matières premières dans l'industrie des engrais et Mg(OH)<sub>2</sub> pour produire MgO utilisé dans l'industrie des réfractaires.*



## 1. INTRODUCTION

Potassium chloride (KCl) is an important product utilized as potassium source in the fertilizer industry. It is usually produced by the beneficiation of sylvinitic ore, a mixture of potassium chloride (KCl) and sodium chloride (NaCl) crystals with some attendant clay and clay slimes, which occurs in evaporite deposits.

The sylvinitic deposit in Brazil are situated in Sergipe and Amazonas. Table 1 shows the reserves in these states.

**Table 1 - Reserves of sylvinitic in Brazil**

DEPOSITS	ORE (10 <sup>6</sup> ton)	K <sub>2</sub> O (10 <sup>6</sup> ton)
Taquari-Vassouras/SE	128.14	30.59
Santa Rosa de Lima/SE	49.50	12.41
Fazendinha/AM	493.00	82.80
Arari/AM	509.00	102.40
	1,116.64	215.29
BRAZIL	1,179.64	228,20

The Brazilian market of potassium chloride is mainly supplied by importation of about 2 million tons/year. In 1986 a potash plant began production in Taquari-Vassouras Basin. Table 2 presents this production. Considering KCl consumption in Brazil and applying a recovery level of 40% to the mining and 90% to the beneficiation, the available reserves are estimated for 50 years.

Table 2 - Brazilian production of potassium chloride

YEAR	KCl (ton)
1986	23,038
1987	62,185
1988	92,888
1989	161,575
1990	111,090
1991	167,776
1992	141,724
1993	288,947
1994	403,904
1995	371,000
1996	440,000
1997	500,000
1998	500,000
1999	700,000

\* prevision

Despite the great potential of potassium ore in Amazonas, the more important deposit of  $K_2O$  in Brazil is from carnallite ( $KCl \cdot MgCl_2 \cdot 6H_2O$ ) in Sergipe. The deposits situated at depths around 200 to 1200 meters are estimated in 24 billion of tons of ore « in situ » corresponding to 2.5 billion tons of KCl.

Camallite is the most abundant potassium mineral in salt deposits and occurs widely in mixture with halite or with halite and kieserite in the form of carnallite ore. Today, however, sylvinite ores are almost exclusively as starting material for the following reasons:

- Camallite ore has unfavorable mechanical properties that make mining more difficult;
- The  $K_2O$  content of pure carnallite is up to 17% compared with 63% for sylvite;
- Whereas the separation and purification of sylvite from sylvinite ore can usually be carried out by flotation, which does not involve a phase change, the extraction ore necessitates dissolution or decomposition of the carnallite, and a high energy consumption for decomposition or purification of the decomposition product, depending on the process;
- The treatment of carnallite generates large quantities of concentrated magnesium chloride solution, which must be disposed off;

For these reasons, mined carnallite ore is today seldom used as a raw material.

The proposed process is based on the ammoniation of carnallite solution to obtain:



After this step, the insoluble  $Mg(OH)_2$  is separated to produce  $MgO$  and a mixture of  $NH_4Cl$  and  $KCl$  which could be used as fertilizer [Cekinski et al (1)].

The goal of this work is to obtain solubility data and the influence of the temperature and pH in the products formed during ammoniation.

## 2. EXPERIMENTAL PROCEDURE

The tests were realized in two steps: obtaining the solubility curves of natural and synthetic carnallite and ammoniation of the solution at different levels of pH and temperature.

### 2.1. Carnallite solubility curve

The crystallizer used was a jacketed glass vessel with a working volume of 1000 ml. It was equipped with a thermometer, a propeller and a condenser to avoid water evaporation. The crystallizer temperature was controlled by circulating water from a programmable constant temperature bath through the jacket.

First, a clear solution was prepared by dissolving 559 g of synthetic carnallite (mixture of reagent grade KCl and  $MgCl_2 \cdot 6H_2O$ ) or natural carnallite in 850 g of deionized water at 25°C. The solution was stirred and cooled until precipitation of material. This temperature was called  $T_c$  (temperature of crystallization). After, the solution was heated at 1°C per hour up to dissolution of all precipitated material. This new temperature was called  $T_d$  (temperature of dissolution). Subsequently, a known amount of carnallite was added to the crystallizer and a new  $T_d$  and  $T_c$  were obtained. This procedure was made up to solution temperature of 80°C.

For the natural carnallite, it was necessary to provide previous filtration of the solution in order to remove insoluble materials, followed by hot water washing of the residue. The clear solution was put in a 60°C oven for water evaporation and subsequent carnallite recrystallization. The main difference between the two carnallites is the presence of NaCl and free KCl in natural carnallite.

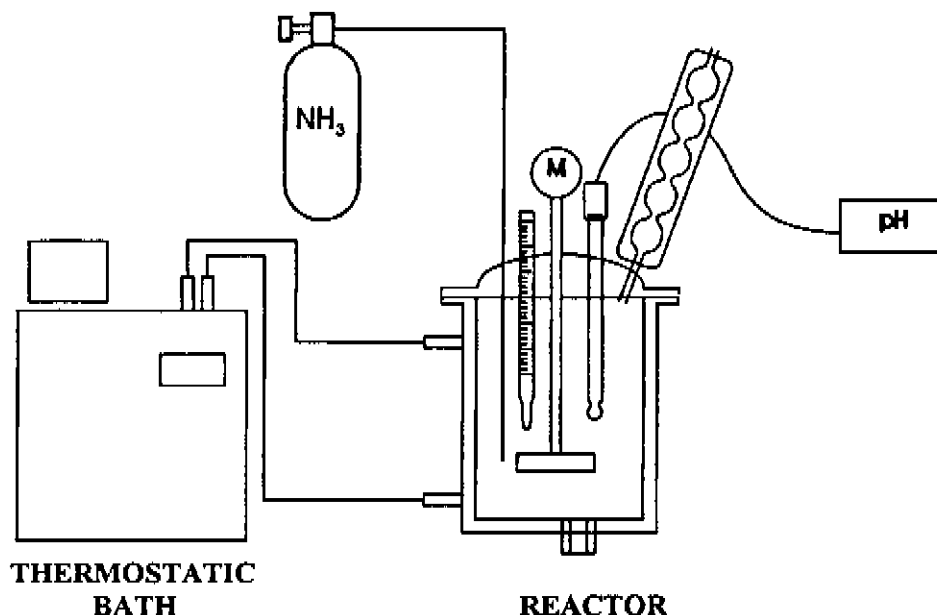
## 2.2 Ammoniation

The reactor used was the same as described above, equipped with thermometer, pH electrode and a system to feed ammonia gas into the solution (Figure 1).

The reactor was filled with 1000 g of carnallite solution according to the solubility curve obtained. The ammoniation of the solution was carried out until it reached the several established pH levels. The studied temperatures were, respectively, 10, 25 and 50°C.

After reaching the desired pH, the obtained precipitate was separated by centrifugation for 30 minutes at 3000 rpm, washed and dried in a oven at 60°C for 24 hours and weighed. The dried material was analysed by X-ray diffraction (XRD) and chemical analysis.

Figure 1 - Schematic representation of the apparatus used in laboratory scale

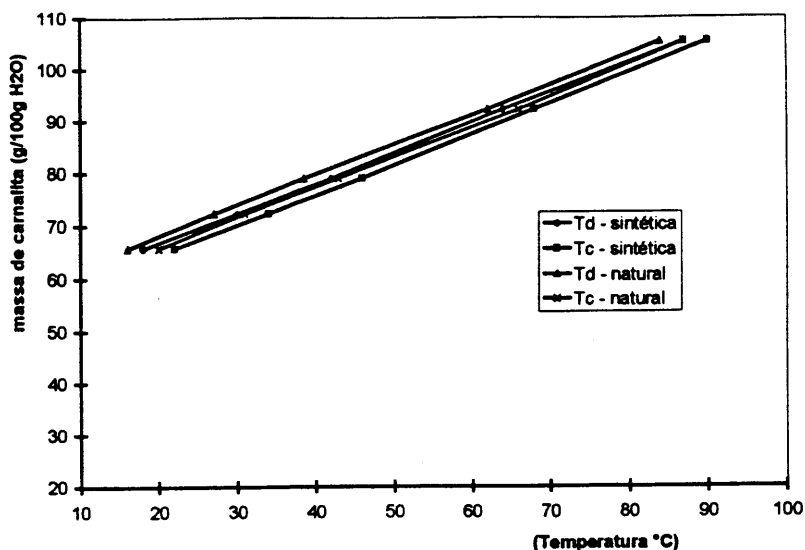


## 3. RESULTS

### 3.1. Solubility curve

The solubility curve results are shown in Figure 2. It is possible to verify that the solubility difference between synthetic and natural carnallite is very small even in the presence of NaCl and KCl present in natural carnallite. The difference between the dissolution temperature and crystallization temperature is also very small.

Figure 2 - Solubility of synthetic and natural carnallite in water



### 3.2. Ammoniation

Table 1 shows the amount of the precipitate produced at each pH level tested.

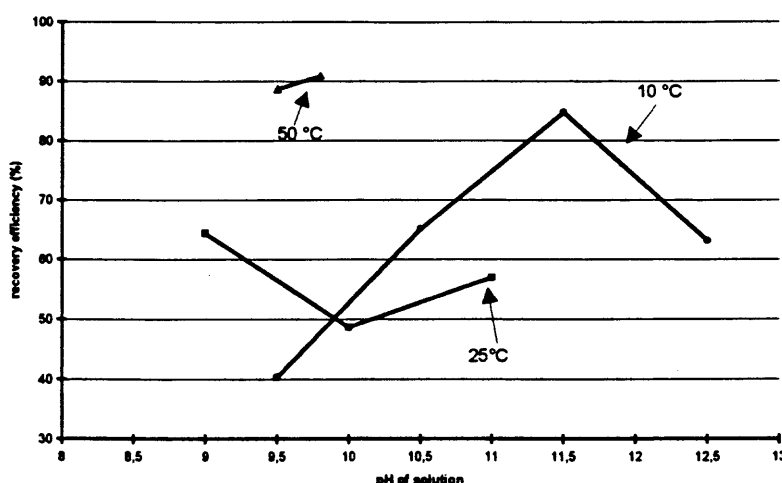
Table 1 - Precipitated amount after ammoniation as function of temperature and pH

CHEMICAL ANALYSIS				Weight of precipitated material
pH	K <sub>2</sub> O	N	MgO	
	(%)	(%)	(%)	(g)
Temp = 10°C				
9.5	5.9	0.8	45.7	45.1
10.5	7.2	1.6	45.6	73.1
11.5	11.3	0.7	40.0	108.3
12.5	13.6	1.3	43.9	73.6
Temp = 25°C				
9	9.19	1.61	39.2	92.5
10	12.6	1.17	30.3	90.4
11	8.65	1.41	33.5	95.7
Temp = 50°C				
9.5	6.7	0.75	45.5	122.4
9.8	11.8	1.65	40.5	141.0

The analysis by X-ray diffraction presented the following crystalline phases: Mg(OH)<sub>2</sub>, KCl and NH<sub>4</sub>Cl.MgCl<sub>2</sub>.6H<sub>2</sub>O, in different proportions for each pH level. However, it should have been small amount of NH<sub>4</sub>Cl and MgCl<sub>2</sub>.6H<sub>2</sub>O in the precipitated material which did not appear in the X-ray diffraction. As 1 g of nitrogen (N) corresponds to 18.32 g of NH<sub>4</sub>Cl.MgCl<sub>2</sub>.6H<sub>2</sub>O, the precipitated material contains a relatively high content of this compound. The values are coherent with the X-ray diffraction.

Based on the chemical analysis results, Figure 3 was made to verify the influence of pH and temperature in the magnesium recovery.

**Figure 3 - Influence of magnesium recovery as function of temperature and pH**



At 10 °C it was possible to work until pH 12.5. At 25°C the maximum pH was 11.0 and at 50°C, 9.8. This was due to the ammonia loss and dissolved salt present in the solution.

At 10°C a maximum recovery of Mg at pH of 11.5 was observed. After this point, the recovery efficiency decreases to 65%. At 25°C, the recovery efficiency begins from 65% at pH 9.0 and decreases to about 50% at pH 10 and increases slightly at pH 11. In the case of 50°C, it was possible to verify only two points. There is a small increase of efficiency of recovery with pH. The different behavior of the curves presented was due to the solubilities level of the dissolved salts which are different at each temperature and pH.

The ammoniation conducted at the temperature of 50°C showed that for the two pH levels, the amount of the precipitate produced, reached the best results. At 10°C the best result was at pH 11.5.

The precipitate obtained after ammoniation were washed with water until total removal of Cl<sup>-</sup> ions, dried at 60°C and calcinated at 1700°C to produce magnesium oxide (MgO).

At the moment, it has been studied the process for recovery dissolved salts from the remaining solution. One possibility is by partial or total water evaporation in order to produce a liquid or solid fertilizer composed by N and K<sub>2</sub>O as primary macronutrients and MgO as secondary macronutrient. The other possibility is the selective crystallization by salting-out with selected solvents, where salt is forced to crystallize by the mutual solubility of water and solvent. After removal of the solid salt, the mother liquor of solvent, water and residual salt are reformed into a regenerated relatively dry solvent phase and a diluted aqueous phase by change in temperature and contact with additional concentrated solution [Weingaertner, et al (2)]. Both phases are directly recycled within the process, allowing creation of a continuous, industrially useful process. The latter process seems more adequate to the process and at the moment the study is been conducted in this way.

#### 4. DISCUSSION AND CONCLUSION

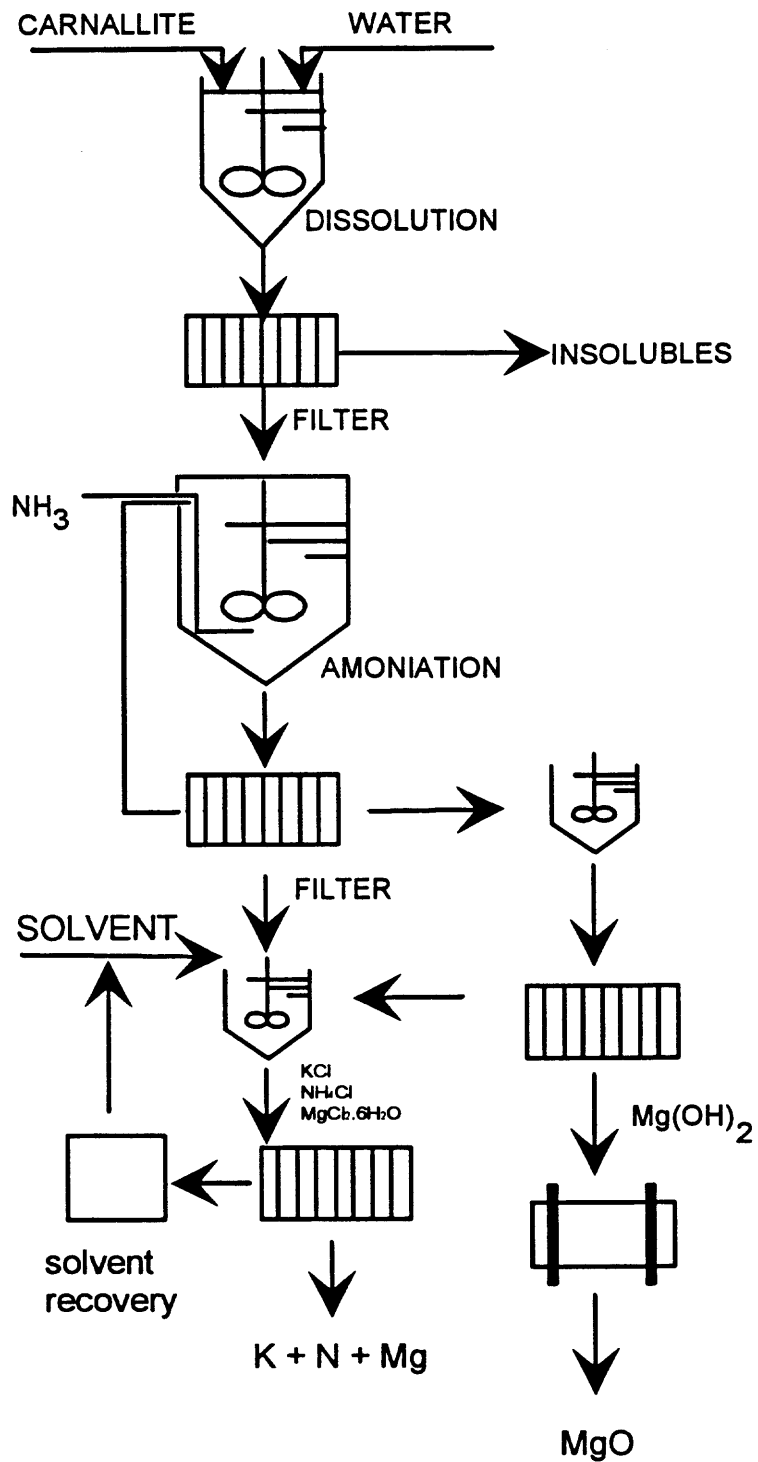
From the present results, it is possible to predict a process according to the flow diagram presented in Figure 4, which could give two types of product: a mixture of nitrogen, potash and magnesium which can be utilized as fertilizer and magnesium oxide, used in refractory industry.

The carnallite is firstly dissolved in water in a dissolution tank. Subsequently, the solution is filtered to remove insoluble materials and sent to the ammoniation reactor where ammonia gas is added. The next step consists of the separation of the insoluble magnesium hydroxide Mg(OH)<sub>2</sub> from the mother liquor by filtration. The separated solid material is resuspended in water for washing, filtered again and sent for calcination in order to produce magnesium oxide (MgO).

In the clear solution, a selected solvent is added in order to recover a mixture of compounds containing nitrogen, potash and the remaining magnesium.

The tests for selection of the best solvents are still in progress and the results up to now have shown that acetone and isopropanol can be utilized for the extractive crystallization of KCl and  $\text{NH}_4\text{Cl}$  dissolved in the mother-liquor.

Figure 4 - Process flow diagram.



## 5. LITERATURE CITED

1. Cekinski, E., Calmanovici, C. E., Valarelli, J. V. Brasil P. I. 8805136 1988.
2. Weingaertner, D. A., Lynn, Scott. Hanson, D. N. Ind. Eng. Chem. Res. 30 490-501 (1991)