Research

Alternatives for the Production of Potassium Fertilizers in Argentina

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ABSTRACT

The use of potassium fertilizers on crops brings with good yields of crops and maximum profitability for farmers. Currently in Argentina, the level of production of potash fertilizers does not cover the needs of the sector making it necessary to import to meet demand. On the other hand, the brines of the Puna, which are exploited to produce lithium carbonate, contain potassium chloride in appreciable concentrations and could be an alternative resource to obtain potassium fertilizer. The aim of this paper is to analyse the possibilities of obtaining potassium fertilizers in the NOA, using both, natural brines and process effluents of obtaining lithium carbonate. Industrially, KCl is obtained by froth flotation and fractionated crystallization. Nowadays, salting-out is not applied industrially to obtain KCl. Through salting-out, KCl crystallization is achieved by adding an organic solvent that modifies KCl solubility. In this work, the three techniques mentioned are compared, focusing on performance, recovery and purity of the crystals obtained. The solids obtained by flotation have purity between 85-90% while by fractionated crystallization the purity of the solids is higher than 95% as in the crystals obtained by salting-out. These results show that the KCl obtained can be used as a fertilizer since it meets the specifications for use as such

Keywords: Potassium; Fertilizers; Brines; Residues

INTRODUCTION

Crops absorb potassium in large quantities, being equal to or greater than even the amounts of nitrogen absorbed. Potassium is vital for the growth and development of plants. It plays a key role in many metabolic processes of plants, it is essential in photosynthesis, optimizes water regulation in plant tissues, leading to increased yields and crop quality [1]. An optimal application of potassium fertilizers is crucial to improve the response of plants, especially to drought, by improving the mechanisms of adaptation and resistance [2].

Potash deposits (soluble potassium salts) are distributed around the world: Canada, Brazil, Germany, Belarus, Jordan, Israel and China. The purest reserves of potash are found in New Mexico (United States of America). The largest producer of potash is Canada, whose largest reserves are controlled by Potash Corporation in Saskatchewan. The countries that consume potash in large quantities are China, the United States, Brazil and India. Brazil imports 90% of its potash consume [3]. World

production of potash in 2017 was 42 million tonnes, and its demand is expected to increase to around 45.6 million tonnes by 2021, with higher consumption in Asia and South America [4].

Considering the increase in population and the associated demand for food, as well as soil erosion, fertilizers in general (potassium, nitrogen and phosphorus) are gaining commodity status. This is because they help to improve soil yields and increase agricultural production [2].

After 2007, the potassium industry sector attracted new interest when world commodity prices doubled [5]. This paper compiles information about the potassium fertilizer market in Argentina. A comparison of feasible production methods from the different raw materials existing in the country is also made.

Potassium fertilizers

Potassium can be supplied to plants using potassium nitrate (KNO₃), potassium sulphate (K₂SO₄) or potassium chloride

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(KCl). Table 1 shows the physicochemical properties of the potassium salts used as fertilizers [6].

Table 1: Physico-chemical properties of potassium salts [6].

Physico-chemical properties	KNO ₃	K ₂ SO ₄	KCl	
%K ₂ O	44-46,3	50-53,5	60-62	
%KCl	36,5-38,4	41,5-44,5	49,8-51,5	
0/ Anim	57,6-60,7 like NO ⁻¹ ₃		45,2-46,7	
% Anion	13-13,7 like N	17-18,2 like S	like Cl	
Saline index	73,6	46,1	116,3	
CE (electrical conductivity) (1g/la 25°C; mS/cm)	1,35	1,54	1,79	
pH standard degrees (10% sol.)	between 8 y	between 2 y 8	7	
pH acid degrees (10% sol.)	between 2 y		•	
Solubility at 20°C (g/L)	316	111	342	

 $\rm KNO_3$ has 46% potassium ($\rm K_2O)$ and 13% nitrogen (N), these are macronutrients completely consumed by plants, leaving no residues of other elements that can be harmful. The synergistic effect between K+ and NO - facilitates the absorption of both ions by the plant roots.

The affinity between negatively charged nitrate and positively charged potassium prevents the latter from being absorbed by soil particles, making it available to plants for a long time [6]. K_2SO_4 contains 50% potassium (K_2O). The SO_4 leaves considerable amounts of sulphate in excess in the soil solution [6]. KCl contains 60% potassium (K_2O). The presence of chloride in the soil affects negatively plants, however, it is possible its use in certain annual crops such as corn, soybeans, wheat and sunflower [6].

Table 2: Solubility of potassium salts at different temperatures.

	Temperature (°C)					
Fertilizer	10	20	30	40	50	
	Solubility (g/1000g water)					
Potassium nitrate	219	316	456	639	852	
Potassium sulphate	93	111	130	148	166	

D	210	240	370	400	126
Potassium	310	340	310	400	420
chloride					

KNO $_3$ has advantages over KCl and K_2SO_4 ; its high and fast solubility makes it an ideal source for preparing fertilizer solutions at any temperature (Table 2). KNO $_3$ is compatible with all fertilizers, while K_2SO_4 should not be mixed with fertilizers containing calcium. The combination between Ca^+ and SO^-2 forms gypsum (insoluble precipitate), which can block the fertirrigation system.

Comparing existing sources in the potassium fertilizer market, KNO₃ offers the following benefits [6]:

- Better nutritional composition for the plant.
- Better performance as a source of K.
- High solubility and rapid dissolution.
- Wide range of compatibility with other fertilizers and agrochemicals.
- Does not interfere with the absorption of other ions by plants.
- Minimal effect on soil pH.
- Low contribution to soil salinity.

However, in Argentina KCl is used as a potassium source, satisfying 39.84% of the demand, the rest is covered by KNO₃ (7.77%), K_2SO_4 (11.3%), potassium thiosulphate (4.41%) and other potassium fertilizers (36.68%) [7].

Several authors studied the effects of K⁺ salts, either alone or combined with other nutrients in various crops [8-11], demonstrating improvements in the physical characteristics of plants as well as agronomic efficiency.

Consumption of potassium fertilizers in Argentina

The crops in Argentina are cereals and oilseeds, being the main: soybeans, corn, wheat and sunflower [12]. As mentioned above, the most used source of potassium comes from KCl, even though it has disadvantages against K_2SO_4 and KNO_3 .

Table 3 presents the K^+ requirements (such as K_2O and KCI) according to the type of soil and crop provided by the NideraNutrientes [13].

Taking into account that KCl covers around 40% of the demand for potassium fertilizers, approximately 4.1 million tons of this salt would be necessary. In general, Argentina has an adequate level of potassium in its soils due to the fact that the types of clays that compose it contain potassium in abundance [14].

Although good quality soils are available in terms of potassium, it can be seen in Figure 1 that imports in the year 2018 for KCl were greater than 25,000 t, while K_2SO_4 and KNO_3 added less than 15,000 t [7].

In 2018, 67% of the consumption of potassium fertilizers by agriculture was imported [7].

The use of potassium fertilizers was, until a few years ago, restricted to intensive productions such as fruit, vegetables and tobacco, and recently some doses of potassium have begun to be

incorporated, especially in areas with many years of cultivation and depleted soils impoverished in terms of nutrient levels.

Table 3: Amount of fertilizer needed, own elaboration from NideraNurientes [13].

C	Regular soil	Seeded	Req. KCl
Crop	(kg K ₂ O/ha)	ha	(x106 t)
Wheat	10	5.341.000	0,712
Soya	100	19.792.100	2,640
Maize	75	6.034.480	0,603
Girasol	100	1.464.855	0,195
Total	285	32.632.435	4,15

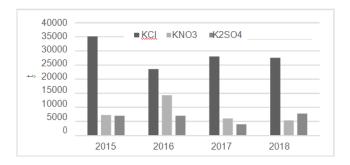


Figure 1: Importation of potassium fertilizers. Own elaboration from CIAFA data [7].

Analysing the Figure 1, it is evident that there is a niche in the market to meet the demand for potassium fertilizers, both nationally and internationally. This need could be covered by taking advantage from Argentina natural resources.

Sources of potassium salts and methods of production in Argentina

KCl salts can be found in brines, underground reservoirs and salt lakes. The most abundant minerals in commercial deposits are: sylvite (KCl), sylvinite (KCl⁺NaCl) and carnalite (K-MgCl₃).

Reservoirs: On the provincial border between Mendoza and Neuquen is the Rio Colorado sylvinite mine. At the moment the exploitation is not carried out due to the suspension of the project. The deposit has a reserve of 300 million tons of KCl; its grade is 28-32% K_2O , with a thickness of 2.2-2.5 m and in some areas with a grade of 20-27% K_2O of 10-20 m thick. Yields of 250,000 t/year of potassium chloride [15] were estimated. The controversy raised by the population is the high amount of water supply (1 $\rm m^3/s)$ and gas consumption required by the process [16]. The mining project is currently being reactivated.

A reservoir of potassium salts can be exploited in two ways. If deposits depths are above 850 m, it is used traditional underground mining. In mineralized zones between 1200 and 2000 m deep, it is chosen solution mining [17]. Potasio Rio Colorado project considers this last alternative.

Solution-mining: This method of production consists of drilling the deposit by injecting water at 60°C through a jacketed pipe. The resulting sludge is extracted by drilling, thus recovering NaCl and increasing the concentration of KCl to saturation point

In the process, petroleum products (insoluble in water) are used as an "insulating fluid" in such a way that it seals the roof of the chamber, avoiding uncontrolled dissolutions in that area and its sinking.

During the dissolution a cavern is formed that grows upwards in a controlled way. In a plant set up to obtain a concentrated brine, the water from the sludge is evaporated (crystallisation stage) and the potassium chloride is separated from the rest of the minerals present in the brine by foam flotation.

Brine: Another source of potassium is brine. These can be divided into two classes: seawater and continental waters (where the salines are found) which are differentiated by the concentration of salts present. The composition of the brine determines the selection and/or design of the processing method. Seawater salt recovery is limited to areas where the climate is dry and warm. In Argentina, salts are not obtained from seawater.

Natural brines are generally saturated in NaCl and have concentrations close to the saturation of KCl. Solar concentration methods are used in combination with industrial recovery methods.

Handmade methods: The traditional methods consist of concentrating the brine by natural solar evaporation. In order to achieve high evaporation, certain requirements are needed, such as, among others, low precipitation, high solar radiation and an important thermal gradient between day and night. These environmental conditions are present in the Puna.

The process consists of a series of evaporation, concentration and crystallization pools. The lithium companies installed in the Puna use this concentration method to condition the brine that they will later use to obtain lithium carbonate. However, the present KCl is not recovered.

Industrial methods

Froth flotation: The method is based on the difference on the hydrophilic or hydrophobic properties of the particles. In most cases, these differences are too small to be used as a basis for separation; this is why the use of certain chemical reagents is resorted to, which are called flotation reagents, whose general function is to highlight the differences in these properties between the components of the ore to be treated.

In the flotation cell, air bubbles are formed. They carry aerophilic particles and due to their lower density they ascend to the surface of the pulp.

The particles that adsorb water (or as it is commonly said, get wet) are called hydrophilic and because of their higher density they sediment at the bottom of the cell. This behaviour depends on the choice of flotation reagent.

Flotation agents are called collectors, modifiers and foaming agents. Collectors are the most important because they modify the surface properties of minerals. The modifiers act by favouring or deactivating the adsorption of the reagents by modifying the pH.

The foaming agent is used to increase the contact surface with the air. If the pulp is kept agitated the hydrophobic particles will adhere to the air bubbles.

Alonso et al. [18] studied the flotation of sylvite both in a natural sample from the Rio Colorado deposit as well as in a synthetic mixture of chloride salts with different cations (such as sodium, potassium, calcium, barium and ammonium). Using the same acetoamine collector in the different assays, they have found that all chlorides float with the exception of NaCl. In the concentrates of sylvite, the other salts exist in low proportion and are also totally solubilised in the carrier brine, obtaining a concentrated sylvite.

Acetoamine salts of n-alkylammonium with a chain length of 12 to 20 carbons are used as selective collectors. They have high surface activity and excellent foaming properties [18,19]. In general, the larger the amine chain, the higher the percentages of recovery and sylvite grade in the concentrate, with less extraction of insoluble impurities.

At the same length of the chain, amines with a lower degree of saturation allow higher KCl grades to be obtained, but with greater extraction of insolubles. According to these parameters, the amines that work best are those with medium collecting power [18]. Another aspect to consider is that long chain amines form colloidal particles [20].

Partially replacing the collector with fuel oil, diesel oil or kerosene reduces fuel consumption by 25-30%. The largest extraction of sylvite is obtained with diesel as it improves the flotation kinetics of coarse particles [21], [22]. Li et al. [23] used kerosene as a collector for the flotation of a KCl from saturated solution in the same, obtaining a recovery of almost 100%.

An improvement of sylvite flotation can be obtained by premixing the foaming agent with the aqueous solution of the collecting amine [24].

By combining the pre-mixing of the foaming agent with the amine or the promoter oil emulsion, it is possible to float both coarse and fine sylvite particles in short flotation columns. The most effective foaming agents are methyl-iso-butyl-carbinol (MIBC) and hexanol [25].

Amines allow a greater selectivity between 15°C and 25°C, since their performance decreases with temperature [19]. According to Alonso et al. [18] the recovery of sylvinite decreases with the increase in temperature due to the fact that the solubility of the acetoaminic collector also increases.

Cao et al. [26] studied the KCl flotation of a saturated solution in NaCl and KCl using different collectors and measured the contact angle of the bubble on the surfaces of the KCl and NaCl crystals, concluding that both cationic and anionic collectors produce a hydrophobic state on the surface of the KCl salt with

finite contact angle values between 30° and 60°, in contrast to the contact angle with NaCl which is zero.

Laskowski and Castro [27] studied potassium flotation in NaCl-KCl saturated brines with the use of long chain primary amines; in this study the equilibrium point between amine and brine is drastically modified due to salt concentrations.

Fractionated crystallization: This method consists of varying the temperature or increasing the concentration of a solution to achieve selective crystallization of a salt. Natural brines in the northwest region of Argentina are saturated in NaCl and present high concentrations of KCl. During the processing of the brine, it is subjected to concentration processes by solar evaporation which allows the precipitation of a mixture rich in KCl. Despite this, this mixture is not currently used industrially.

Salting-out: The process known as "salting-out", "drowning-out" or "dilution crystallization", allows the separation of salts from an aqueous system by the addition of a miscible component in water, capable of changing the solubility of the solute.

It is a necessary condition that the salting- out agent is more soluble in the original solvent than the solute, so that it can displace it from the solution [28].

In this method it is possible to selectively precipitate salts from a completely miscible mixture formed by the solution, from which it is desired to precipitate the salt, and the salting-out agent.

This technique is known in the pharmaceutical, biotechnological and food industries as it allows the separation and purification of enzymes, proteins, peptides, etc. [29-32].

The salting-out and phase separation effect for aqueous solutions of different electrolytes and organic solvents was studied by various authors [33-37] with the aim of controlling and analysing the size of the particles obtained as well as their nucleation.

Another option for separating potassium salts from brines is to transform KCl into another salt, such as KH₂PO₄, and to separate it by a salting-out process using ethanol or propanol as salting-out agents [38,39].

Argentinian North-west production possibilities

One of the great investment opportunities for obtaining KCl in Argentinian northwest are the brines, which mainly contain sodium, potassium, lithium, magnesium and calcium salts, as well as borates, sulfates and carbonates.

In general, the brines present in Argentinian salars are saturated in NaCl and highly concentrated in KCl. These deposits are located in salt flats where climatic conditions allow the concentration of brines by solar evaporation. The Puna of Argentinian northwest is a region where different salts are currently exploited to obtain refined lithium products (Li₂CO₃ or LiCl).

Among them, the salt flats of Diablillos and the salt flats of Hombre Muerto would be very good sources for obtaining potassium salts since they have concentrations of around 750ppm of K⁺ and the necessary facilities (electricity and gas).

The methods used to obtain refined lithium products differ from one company to another, but independently of them, the residual brine is highly concentrated in KCl (about 2-3 g of K⁺ per 100 ml of brine).

From the depleted brine (depleted in Li⁺ or residual brine) potassium can be recovered as KCl or as another potassium salt by adding the corresponding reagents.

The processes for recovering potassium from the brine may involve, among others: selective crystallization, evaporation and subsequent cooling, foam flotation and salting-out. Our work group performed evaporation and cooling crystallization tests, as well as foam flotation. Natural brines and Punasylvinite were used as raw material.

In the case of brines, the degree of evaporation required to saturate the brine in KCl depends on the initial composition of the brine. Our results show that it is necessary to evaporate around 60% of the water to start obtaining KCl crystals. Figure 2 shows the spectrum of the mixture obtained. By chemical analysis it was determined that the solid contained about 80% w/w NaCl and 22% w/w KCl (Table 4).

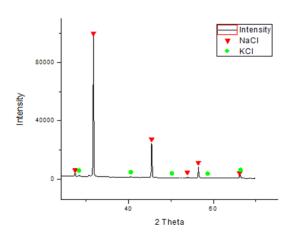


Figure 2: XRD of the solid obtained at 60% evaporation of water.

Table 4: Shows the variation in the natural brine composition as the water evaporates. The initial composition of the natural brine corresponds to 0% evaporated water.

Composition of brines (%w/v)										
Water (%)	evaporated	Na ⁺	K ⁺	Li ⁺	Mg^{+2}	Cl	SO -2 ₄	B ₄ O ⁻² ₇	Dry solids (% w/w)	Density
0 (initial)		7.2	0.75	0.08	0.18	12.01	0.76	0.21	23.57	1.13
10.5		8.35	0.78	0.09	0.22	14.2	0.9	0.24	26.605	1.15
20		9.44	0.95	0.1	0.24	16.22	0.96	0.24	29.34	1.16
29.7		11.38	1.15	0.11	0.27	18.63	1.09	0.24	34.285	1.15
50.1		11.25	1.7	0.2	0.4	19.94	1.45	0.28	38.345	1.16
59		9.13	2.41	0.27	0.76	20.65	1.98	0.28	36.11	1.2
60.6		8.92	2.61	0.24	0.6	20.4	1.96	0.28	38.42	1.21
68.78		9.07	3.2	0.34	0.82	20.13	3.76	1.23	39.02	1.23
70.14		8.24	3.87	0.4	1.1	20.73	2.95	0.31	40.76	1.23
75.4		7.38	4.5	0.48	1.24	20.4	4.78	1.71	42.57	1.25
80.09		4.89	4.47	0.44	2.3	19.36	5.55	0.31	45.83	1.27
82.74		5.15	5.21	0.81	2.14	19.7	7.87	2.95	47.28	1.28
88.47		1.9	2.89	1.01	4.57	21.79	6.11	2.28	47.97	1.28
91.8		0.47	0.59	1.43	6.05	27.54	3.67	1.73	51.29	1.27
93.7		0.09	0.04	2.54	7.37	33.51	1.15	2.76	84.36	1.32

When the 60% of evaporated water is exceeded, potassium salts begin to precipitate along with NaCl, so it is necessary to look for a method to separate these two salts. KCl can crystallize from a saturated solution by controlled cooling [40].

RESULTS AND DISCUSSION

One of the methods of separation of KCl from saturated brines in NaCl and KCl is by fractional crystallization. This separation procedure consists of varying the temperature of the solution in such a way as to modify the solubility of the salts present. Crystallization tests were performed at atmospheric pressure.

The difference in solubility between NaCl and KCl at different temperatures was taken into account [41]. A synthetic solution saturated in KCl and NaCl was prepared (reagents p.a., Cicarelli® brand and distilled water were used, in stirrers at a speed of 350 rpm) so that the crystallization of KCl could be studied at 5, 20 and 80°C.

Table 5: Concentration of the solutions and the solids obtained at each stage.

Composition (% w/w)								
Initial (%p/v)	· • · · ·		Solution (%p/v, step					
NaCl	KCl	NaCl	KCl	NaC 1	KCl			
		18.57	23.08	17.8	7.72			
24.61 12.74	Hot crystal (80°C, step 1)	Cold crystal step 2)	(5°C,					
		NaCl	KCl	NaC 1	KCl			
		71.1	30.2	2.57	98.27			

In the first instance, work was done at 20°C. This saturated solution was heated at 80°C (step 1); due to NaCl is less soluble at 80°C than at 20°C this salt precipitate.

On the other hand, KCl solubility increases with temperature; in consequence an amount of this salt was added to assure that the solution is saturated in both salts at 80°C.

The crystals obtained were separated at 80°C by filtration. These crystals, obtained at high temperature, are characterized by their purity in NaCl. Subsequently, the filtered solution was cooled up to 5°C (step 2); the crystals obtained after cooling were filtered at the same temperature.

Sodium and potassium in both, solids and solutions were analysed by atomic absorption spectrophotometry with Shimadzu AA-6501F hollow cathode lamp. The results of this

fractionated crystallization process are shown in Table 5, being the solid of interest the one obtained at low temperatures.

With this method, the purity of the KCl obtained at the end of the process is higher than the commercial specifications and the NaCl content is lower than that reported by the commercial brands of potassium fertilizers [42]. When working with p.a. grade substances, it is considered that an XRD analysis is not required.

Traditionally, KCl is concentrated by foam flotation as it was already sand. This process requires the pulp to be conditioned with specific collecting reagents.

The froth flotation tests were carried out at constant temperature and pressure. Two froth flotation tests were carried out in two stages in flotation cells, for which a pulp was prepared using a solid mixture of 19-22% w/w NaCl and 60-62% w/w KCl from the salt (Table 6) and a saturated solution in NaCl and KCl at 20°C (reagents p.a., Cicarelli® brand and distilled water, were used in agitators at a speed of 350 rpm).

The concentration of solids in the pulp was 27%. A mixture of amines at 2% w/w was used as surfactant in both tests; the second one is differentiated by the use of Guar Gum at 0.5%. The amine dosage was 100 g/t and Guar Gum 60 g/t. Amine conditioning time was 7 minutes and Guar Gum 1.5 minutes.

The frothing time in both trials was 3 minutes and 10 g/t was used as methyl iso-butyl carbinol (MIBC) frothing agent. The flotation trials were performed following the procedure used in a private company, so no information can be given about them. Cold water $(5^{\circ}C)$ was used to wash the crystals (leaching), taking advantage of the low solubility of KCl at low temperatures.

Another procedure to obtain KCl that was carried out was salting-out. For this purpose, a synthetic solution saturated in NaCl and KCl was prepared at 20°C and atmospheric pressure (reagents p.a., Cicarelli® brand and distilled water were used, in agitators at a speed of 350 rpm).

The saturated solution was mixed with ethylic alcohol. The alcohol modifies the solubility of the salts in the solution, causing the instantaneous precipitation of the KCl mixed with a smaller amount of the NaCl.

Several concentration of alcohol was tried (between 10 and 80% v/v). The best results were obtained at 20% v/v. Purity between 95-97% w/w of KCl was obtained, so it can be used as a fertilizer since it reaches the market specifications.

Table 7 shows a comparison of yield, recovery and purity, obtained in the three methods performed. The yield was calculated as the ratio of the amount of solid obtained over the initial amount of solid.

Recovery was determined as the amount obtained of KCl over the initial amount of KCl. In terms of yield, the results of the salting-out test are comparable to those of the froth flotation and crystallisation tests. Comparing the three methods, higher purity is obtained by salting out.

Table 6: Concentrations of the solids mixture of the froth flotation tests.

Pulp concentration (% w/w)				% w/w KCl				
Test Number	%KCl	%NaCl	% M~C1	1st stage		2nd stage	2nd stage	
%RCI		%NaCl %MgCl ₂		Floting	Sunken	Floting	Sunken	
1	22,45	60,6	4,6	75.9	10.1	78.8	37.3	89.9
2	19,75	61,15	2,9	74.2	10.4	77.4	29.8	87.7

Table 7: Comparison between the different methods of obtaining KCl.

%	Efficiency	Recovery	Purity
Froth Flotation	16-Oct	40-69	87-89
Crystallization	9,6	56	98
Salting-out	6	51	95-97

CONCLUSION

There is a niche in the national market for the commercialization of potassium fertilizers, which today is covered by imports but which could be supplied by national production. Argentina has important sources of brine from which different potassium salts could be extracted. Currently the salt flats are being exploited to obtain refined lithium products. The residual brinesof the processes of obtaining these products are an important source from which potassium salts could be obtained. The results of the tests carried out show that it is possible to separate KCl from NaCl saturated solutions. The salting out is an effective KCl separation alternative. The advantage of this method over traditional methods is that low-cost reagents are used at room temperature.

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