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Experimental study recovery potassium by leaching a mixture salt Halita-Silvita, using saturated brine halite agent leached like

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Abstract

The lithium carbonate, presents an increase in price and demand, however, there is not studies where an equation is proposed that allows modeling the Chilean exported behavior of the mineral. This study is put forward an equation that allows to model the lithium carbonate exports in addition to identify the most influence variables in the commercial exchange of that product between two countries, using the extended gravitational model. The estimated model is not consistent with the gravitational model theory. This is because lithium carbonate is a manufacturing input and the costs of transporting and importing do not influence the volume that is imported. This research has opened new study proposal; such as improve the lithium carbonate export estimation taking into consideration the problem of zero observations.

Keywords: Chile; Lithium Carbonate; Export; Gravity Model.

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I.INTRODUCTION

At the Salar de Atacama, potassium chloride is currently produced using a brine concentration process that is extracted from the salt, precipitating salts through the use of solar evaporative pools, selectively by fractional precipitation, obtaining in the first pools of the evaporation string a mixture of salts with a high content of Halite (of the order of 80 to 90%), the remainder being gypsum and silvite (KCl). The pools that lead to the production of KCl are also used in the production of lithium-rich brines, which are subsequently processed to obtain chemical carbonate or lithium hydroxide plants. The process generates Halita discards, which are calculated in several tons. These preparations have their origin in Halita pools which originate salts with potassium grades between 1 and 9% w / w. The typical composition of these discard salts consists of Halite with laws in general of over 90% and gypsum (CaSO_4·H_2 O) or anhydrite (CaSO_4) in percentages below 3% in general (depending on the characteristics of the brine composition fed in pools) . In all these cases the salts are discarded and collected as discarding salts, generating waste dumps. In some of them its average law is known and in others, in general, there is more uncertainty.

The mining leaching process is known and widely used. It is used in Chile in copper mining and nitrate processes, with appreciable crystal sizes of about ¼ ”to ¾” , while a Halca salt from Atacama to leach does not exceed 0.5 cm in size and responds to other properties, which does not make them comparable. This means that irrigation rates other than those observed in leaching processes of other types of mining input are expected. This paper presents a study of potassium recovery by leaching Halita salts with fixed laws of 7% by weight of K in the salt from saturated brines in Halita. The brine is made from commercial salt and distilled water. The salt is prepared with commercial salt and potassium (KCl) in analytical grade. The study contemplates an experimental work of piloting leaching columns between 0.5 m -1.8 m high at a known temperature. It is expected that the higher the column height, the better the recovery of potassium.

It is proposed to work with three different irrigation rates of the order of 2.4 lt / hr - 3.6 lt / hr - 4.8 lt / hr in columns of variable height, whose heights defined for the study are the following: 0.5 m - 0.8 m - 1.3 m - 1.8 m. In this way twelve experiments are performed. With this information, we want to evaluate how efficient potassium recovery is in different cases.

In the Atacama salt flat, the companies that produce potassium, have a production process of KCl (potassium chloride), which consists of a train of pools whose objective is to evaporate water by solar radiation so as to selectively precipitate salts. Solar pools are classified by different names according to the salts that precipitate. The first of these are the “Halita pools” in which salts with potassium laws of up to 9% p / p originate.

Subsequently, a combination of KCl/NaCl is selectively precipitated with a relative weight ratio of the order of 30% / 70%. However, in both pools (Halita and Silvinita) salts are observed that are in the transition in law of both pools. There are salts that are obtained in Halita pools with appreciable potassium contents (of the order of 5% in K or less) and others in Silvita pools that fail to satisfy the law required by the flotation process. This is due to the fact that solar pools are chemical reactors open to the atmosphere that in the desert have great thermal oscillations of day and night. These oscillations can be 40 °C. The solubility of Halite is not very sensitive to temperature, but the solubility of Silvita has a strong dependence on this variable, generating a loss of sensitivity in the control of salt production.

Salts that satisfy laws greater than 9% K are destined to a flotation plant to separate both salts and obtain a salt rich in potassium with a law greater than 90%, once the concentration process is completed. Those salts that have problems , since it does not satisfy the law that requires potassium for its subsequent separation in the plant are discarded and collected as salts . The present work deals with artificially created salts, type Salar de A tacama, with a fixed grade of 7% by weight of potassium assuming the rest of the salt exclusively as Halita (the plaster or anhydrite is neglected as components).

It works with salts whose sieves are chosen in the range of mesh values # 1/4 to # 5 what is commonly known as «coarse salt». A stockpile of a salt flat can contain agglomerations of large salt or rocks inside (in particular the larger collections of large size), since they have received scabs from the salt that corresponds to raw material of other characteristics. It could be of the order of 10% of the total. This can reduce yields in a salary. The case under study is not intended to simulate leaching of preparations in exact conditions to that found in the productive tasks of the Salar de A tacama, but rather proposes a study of controlled variables where an intellectual exercise of the problem is considered.

Since potassium cation is more soluble than sodium cation at high temperatures (see table 1), temperature is expected to be a variable that affects leaching recovery [1]. It is proposed to work at room temperature, where both solubilities are comparable and by this, estimate the recovery of potassium using leaching as a recovery route. The motivation to achieve this potassium is to recover brine with a high content of this element which can subsequently, using evaporation routes, become Silvita (KCl) that qualifies according to its law, to be processed in the flotation plants that separate NaCl of KCl (grade greater than 9% by weight of K). The effect of the plaster is ruled out given its low grade and its small solution solubility (insoluble salt).

For this study there is no more bibliographic information regarding the treatment of these salts with leaching. Só there is reference books and articles that realize the process, construction and operation of solar ponds, design and control variables, which does not deliver more than some general background of these salt flats and their production processes. This makes this type of study a contribution to the understanding of these systems [2, 3, 4, 5].

The experiments are carried out in the mining laboratory of the San Sebastián University and the potassium law is quantified in the solutions with potassium ion selective electrode sensors. The salts are prepared by measuring the weight of Halita salt independently of the Silvita salt. Anhydrous salts are used.

2. Methodology

2.1 Description of the assembly and the experiments to be performed

The project consists of a study of potassium recovery by means of leaching Halite salts with laws approximately 7% by weight of K in the salt contained in the column from a brine leaching agent saturated in NaCl.

For this, it is proposed to work with coarse commercial salt and potassium chloride (KCl), creating with both a mixture, in analytical grade, that will be used as a material to leach that is located within the leach column. The brine, the leaching agent in this case, is made from commercial salt and distilled water to the point of saturation of the salt in the liquid.

The study contemplates an experimental work of piloting leaching columns with heights of 0.5 m - 0.8 m - 1.3 m - 1.8 m at a known temperature, in addition it is proposed to work with 3 different irrigation rates of the order of 2.4 lt / hr , 3.6 lt / hr and 4.8 lt / hr. In this way twelve experiments are performed.

With this information it is desired to evaluate how efficient the recovery of potassium is in the different cases proposed, for this it is proposed to achieve the results of the leaching process by means of an analytical measurement equipment, which in this case is that of reference electrodes which we it will allow to obtain the concentration of potassium contained in the brine extracted from the column or called, in case of leaching, PLS (Pregnant leaching solution).

2.2. Equipment

2.2.1. Leaching Columns

In the mining laboratory of the Universidad San Sebastián there is a leaching column 1.8 meters high and 4.6 cm internal diameter. This column is made of acrylic and is attached to a metal structure, which allows the column to be held and the equipment to be manipulated, in order to add the hose to distribute and transfer the flow to the top of the column, when mounting a pump peristaltic that allows the feeding of the column, located in the lower part of the assembly. At the bottom, the column has a stopcock to allow the PLS solution to be extracted.

The assembly and location of the equipment is shown in figure 1, the pump used in the process is also added in figure 2:

2.2.2. Potassium measuring equipment (potassium selective ion sensor)

The equipment to be used is the HI 5222 research grade meter, of the HANNA Instruments brand. It is a research meter with double channel and two independent inputs for pH electrodes, ORP and selective ion electrode, and also measures pH, mV, temperature and through the reading of electrical conductivity, gives us values of resistivity, salinity and total dissolved solids.

2.2.3 Determination of Heights, masses and volumes of salt in the s columns

The material used corresponds to commercial salt of coarse size which is screened in # 3/8, # 1/4, # 5 and # 100 meshes. This has a defined granulometric size as material retained in # 1/4 and # 5 meshes is used. The percentages retained in the meshes correspond to the following: # 1/4 is around 20%, in the # 5 mesh it is retained by 40%, while in the # 100 mesh 40% is retained but for this experimental process This particle size will not be studied, so it is discarded. In the mesh # 3/8 it was decided to pass all the material. Once the size to be used is known, the next step is to calculate the amount of material to be used in the columns, through theoretical calculations, for the different heights in which you want to work. For this it is important to know the volume presented by the column to be used, since the only variable value in this calculation is the height.

To make the experience as accurate as possible, the theoretical calculation of the amount of KCl that is part of the mixture respecting the law of 7% is performed K in s columns.

$\%\ KCl=(7\%\ en\ K)/(39{,}102\ gr/mol)*(39{,}102\ gr/mol+35{,}453\ gr/mol)=13{,}35\%\ KCl$

The result obtained is the percentage by weight of KCl, which must have the total mass of the mixture . The Table 2 realizes the ratio mass of NaCl and KCl in the four columns possible that can be assayed at different heights, as is chosen 50 cm, 80 cm, 130 cm and 180 cm heights experiment:

2.3. Preparation of salts to load columns and data acquisition

With the column loaded and the pump installed, the saturated NaCl solution is prepared, which is the leaching agent. For this, fine commercial salt and distilled water are available.

The PLS obtained from time to time will be measured in specimens and stored in plastic bottles for samples that have an approximate volume of 100 and 200 ml. These samples are labeled indicating nu number of order, time of operation, high salt in the column, flow supplied brine , vol Total umen removed in recovery time, mass of NaCl and KCl, Height experimental salt , flow supplied with brine and ambient temperature at which the column is operating.

A below in Table 3, disclosed the 12 experiments to be performed, including you mperaturas and irrigation flows which are operated:

2.4. Measurement of potassium concentration using selective ion electrode

After having all the data and samples of the 12 columns run, the amount of potassium recovered in the samples is measured. The method to be used in this case is that of potentiometry, in which it consists in determining the concentration of a species using reference electrodes. This requires the potassium ion selective electrode, their respective ISA and ISE (in this case potassium), beakers, test tubes, pipettes and electronic equipment, which shows on its panel the concentration that has been obtained in the sample. To carry out the measurements, the equipment is available, and for this purpose the samples taken, in the leaching process, must be poured into a beaker for measurement. Configuring the equipment is of vital importance, since it must be calibrated with standard ISE solutions, which are solutions with a known concentration of the element to be measured. To calibrate, four solutions of different concentration are required to create a calibration curve that helps interpolate the measurement of the sample, for this there is a standard solution of 0.1 Molar of Potassium. As four solutions are required, three more solutions are created with 0.01M, 0.001M, 0.0001M concentration using distilled water and dissolving the 0.1M solution. Check before the calibration is in the corresponding unit of measure, in this case, Molar. Calibration is performed from lower concentration to higher concentration using the keypad on the equipment panel. After calibration, the unit of measure of concentration of the equipment for which you want to work must be changed, this time the standard measure “grams per liters” is used. To measure the samples it is required to add 2 ml of ISA solution per 100 ml of sample, the objective of this solution is to stabilize the element to be measured in the sample.

3. Tabulation of experimental data and results

In each of the twelve leaching experiments, potassium concentration data recovered using the potentiometry method with potassium selective ion electrodes are obtained. The details of the mentioned data are disclosed below describing column by column.

3.1 Example of calculations in the first experiment (Column 1)

The height of this column is 50 cm, for this a mass of 782.2 g of NaCl and 121.9 g of KCl is required, which are data calculated previously in Table 3. With that amount of KCl, respecting the law of 7% of K, theoretically, 64 gr of potassium should be recovered. To this column is supplied one flow of 2, 4 l/h of saturated brine. Next, in table 4, a series of relevant data are presented in the sample measurement process.

The Tables 5 and 6 , reflect the data in column 1, in which the used amount of accumulated volume of brine to the amount of potassium recovered accumulated in grams as passed the process shown (Table 5) and the percent recovery obtained with respect to l at the rate of leaching (Table 6).

Below are graphs obtained for column 1, with the previous data, in Figures 3.

As can be seen in Figure 3, at the beginning, the recovery curve grows rapidly, obtaining that the vast majority of K, approximately 50 gr, is recovered at the first litre of brine supplied. Then the curve begins to tend to the asymptote that is expected to be 64gr of potassium and the recovery is much lower using a large amount of brine.

In figure 3, it is observed that the curve shows considerable growth at the beginning of the process, which can be concluded as a great recovery, around 80% at a leaching rate of approximately 1. Then the recovery decays and you get the process recovery, but smaller and presumed to be at a great cost. Finally, it can be seen that the leaching process obtained a recovery of 97.3%. The same analysis can be done for each experiment in the twelve columns by reporting each of the results of the twelve experiments. To avoid reporting each experience, a summary is presented with the main results below.

3.2 Graph comparison

One of the objectives of the experiment is to be able to compare the leaching processes at different heights and flows, so, after performing all the leaching columns, taking all the samples, quantifying the recovery of potassium K, and graphing with the data obtained from the measurements of the samples, it is necessary to compare the different constructed graphs with a variable in common. Therefore they made the following representations:

3.2.1 Graphics of different heights, same flow.

In Figure 4 , it can be seen that the column with greater height obtains a greater percentage of recovery of the salt of interest with a lower leaching ratio with respect to the other heights, this due to the greater height there is greater brine interaction / salt and also longer residence time of the brine in the column.

Figure 5 , it is perceived that also the column with greater recovery remains the highest, in this case, the difference to Figure 4, is that the leaching ratios are greater, and this is because more flow was supplied , but behaves the same way. Curves almost rectilinear vertically that then decay at some point where the recovery is less to greater leaching ratio. It can also be said in Figure 5 , that the higher the column height, the less leaching reason is due to the fact that perhaps the residence time of the brine in the salt is greater than the brine / salt interaction allows the greatest recovery with less leaching ratio.

In figure 6 the same action is contemplated as the graphs of the previous figures. Taking the column with greater height to have greater recovery of K during the process with respect to the leaching ratio, making it clear that the same recoveries are had in all the columns, but at a lower height, more brine used, which is It translates to less profitability.

The column of greater height allows a greater recovery with less leaching ratio may be due to the longer residence time of the salt in the brine, so it allows greater interaction between brine / salt helping to obtain a higher K.

3.2.2 Graphics of different flow, same height

In Figure 7, it is observed that the column that presents the least flow is the one that allows the highest obtaining of K in the process, also at a lower leaching rate. It allows a recovery of close to 80% at a leaching ratio close to 2. With respect to the variation in the leaching ratio, it can be deduced that there is more reason for leaching due, clearly, to the flow since a higher flow is used more brine, which would cause an excessive expense of this, since when much of the potassium has been recovered it will continue to flow obtaining little recovery. It should be remembered that 20%, 30% and 40% in flow translates to 2.4 lt / hr , 3.6 lt / hr and 4.8 lt / hr of saturated brine halite irrigation supplied to the column by the pump .Figure 8 . Comparative graph with height 50 cm and different flow.

The Figure 8 , also shows that recoveries are identical, but that higher flow rate is greater leaching, because the time of brine / salt interaction is very low, which makes waste brine. The recovery in this case is approximately 85% with a leaching ratio close to 1, in the case of lower flow.

The Figure 9 discloses that lower flow higher recovery is obtained, the edge is 95%. It also indicates that it has a lower leaching ratio because the flow is low. The high recovery with respect to the low leaching ratio can be caused by the fact that it has a longer residence time in the column, which allows a greater interaction between brine/salt. Also saying that brine is wasted at a higher flow due to the low interaction that can cause the column, allowing a lower recovery value.

In Figure 9, it is shown that the recoveries are similar, but detailing, again, that at a higher flow the potassium recoveries are lower. Due to what has been explained above, which is the low residence rate that occurs, causing the brine / salt interaction causing the recovery curve to fall v / s leaching ratio. It can be seen that at a rate close to 1, the columns show deviations, as mentioned above, causing excessive brine expenditure in leaching.

Table 1. Solubility of pure compounds

Solubilidad de compuestos										
Temperatura	**0^{oC}**	**10^{oC}**	**20^{oC}**	**30^{oC}**	**40^{oC}**	**50^{oC}**	**60^{oC}**	**70^{oC}**	**800^{oC}**	**90^{oC}**	**100^{oC}**
Nacl(*)	35,7	35,8	36	36,3	36,6	37	37,3	37,8	38,4	39	39,8
(*) Cantidad de sustanica anhidriha (gramos) que es soluble en 100gr de solucion a la temperatura indicada en grados centigrados											

Source: CRC Handbook of Chemistry and Physics, 85 edition, CRC Press, Florida, USA. Lide DR, (2005)

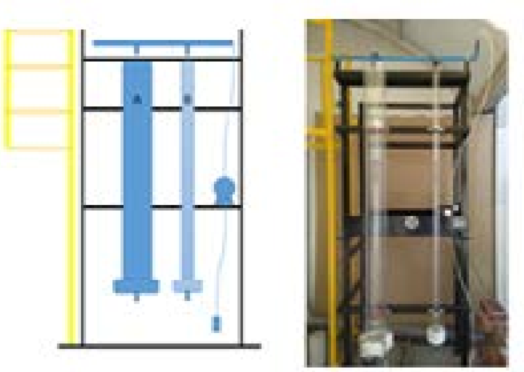

Fig. 1 Leaching column assembly

Fig. 2 Peristaltic pump

Table 2. Amount of KCl and NaCl per column.

Masa por porcentaje de KCL y Nacl (kg)			
Altura (cm)	**Masa total en columna**	**Masa de KCI**	**Masa de Nacl**
50	0,902	0,120	0,782
80	1,444	0,193	1,251
130	2,346	0,313	2,033
6180	3,249	0,434	2,815
	Total	1,060	6,881

Table 3. Experiments with their respective heights salt column temperatures of operation.

Experiment No.	Salt Height (cm)	irrigation flow (lt / hr)	Temperature (° C)
one	fifty	2.4	39
two	80	2.4	44
3	130	2.4	37
4	180	2.4	37
5	fifty	3.6	38
6	80	3.6	39
7	130	3.6	39
8	180	3.6	44
9	fifty	4.8	44
10	80	4.8	41
eleven	130	4.8	40
12	180	4.8	38

Table 4. Data obtained from column 1.

N°Orden	Concentraction de k en muestras (gr/lt)	Error en	Vol. muestra	Error Vol.	gr Potasio Total en muestra	Error gr K
1	14,11	2,12	170	5	23,98	3,67
2	5,86	0,88	190	5	11,13	1,70
3	4,34	0,65	190	5	8,26	1,26
4	2,22	0,33	190	5	4,22	0,64
5	1,00	0,15	170	5	1,71	0,26
6	0,70	0,10	120	5	0,84	0,13
7	0,50	0,07	400	5	1,99	0,30
8	0,38	0,06	410	5	1,55	0,23
9	0,33	0,05	400	5	1,33	0,20
10	0,25	0,04	770	5	1,93	0,29
11	0,20	0,03	810	5	1,64	0,25
12	0,19	0,03	770	5	1,47	0,22
13	0,17	0,03	800	5	1,34	0,20
14	0,13	0,02	680	5	0,88	0,13
			gr total K:		62,25	

Table 5. Column data 1. Cumulative volume of brine used and cumulative amount of grams recovered from K.

N°Orden	Volumen acumulado (ml)	K acumulado (gr)
1	170	23,98
2	360	35,11
3	550	43,37
4	740	47,39
5	910	49,30
6	1030	50,14
7	1430	52,12
8	1840	53,68
9	2240	55,00
10	3010	56,93
11	3820	58,56
12	4590	60,03
13	5390	61,37
14	6070	62,25

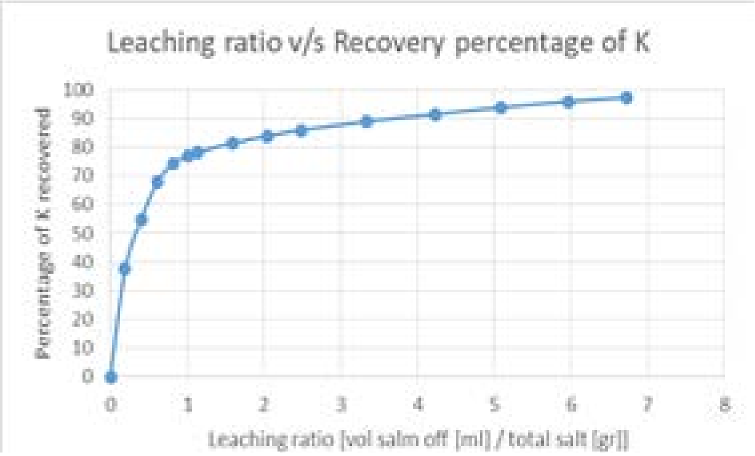

Fig. 3 Leaching ratio v/s recovery rate of K

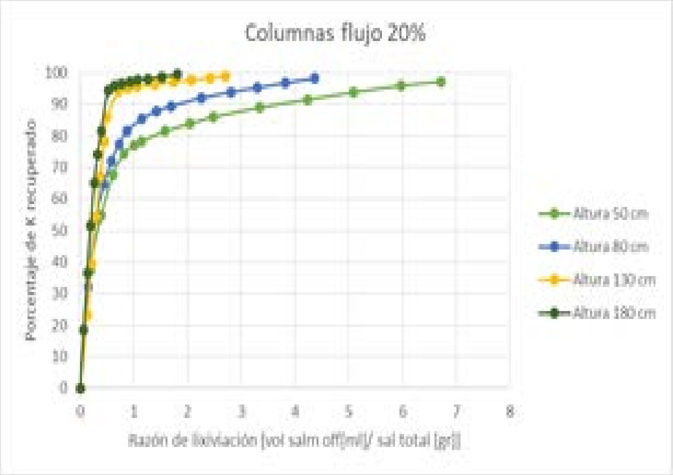

Fig. 4 Grafico comparison with flow 2.4 lt/hr (20% of peak flow pump) and different heights

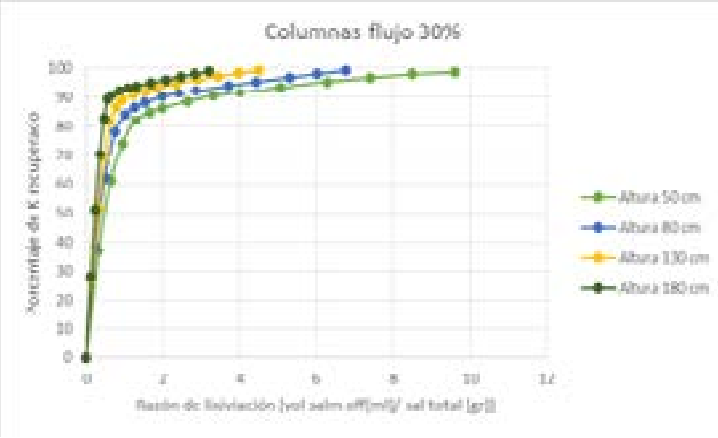

Fig. 5 Comparative graph with 30% flow (3.6 lt/hr) and different heights (cm)

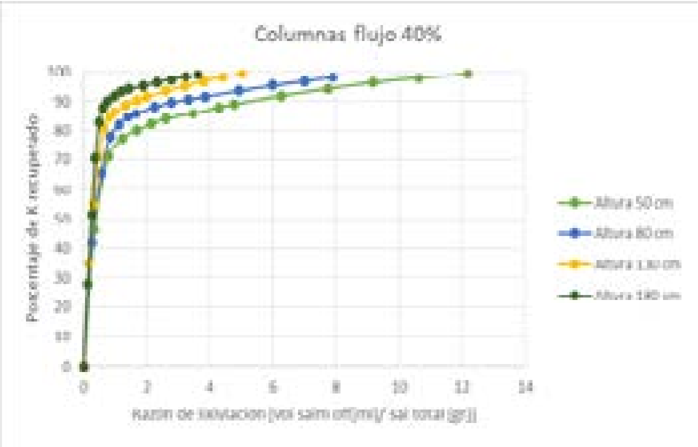

Fig. 6 Comparative chart with 40% flow (4.8 lt/hr) and different heights

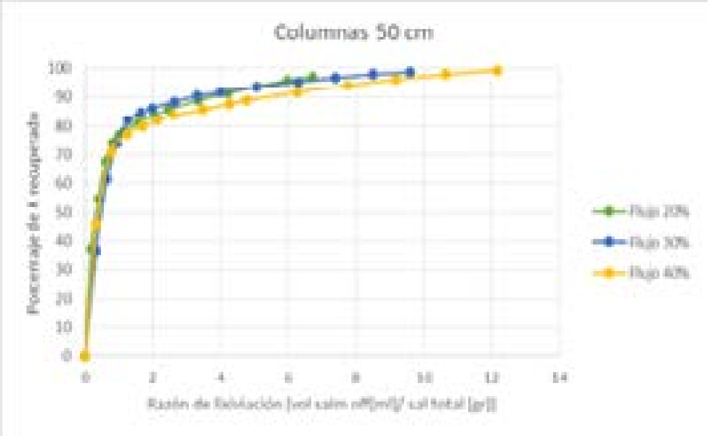

Fig. 7 Comparative graph with height 80 cm and different flow

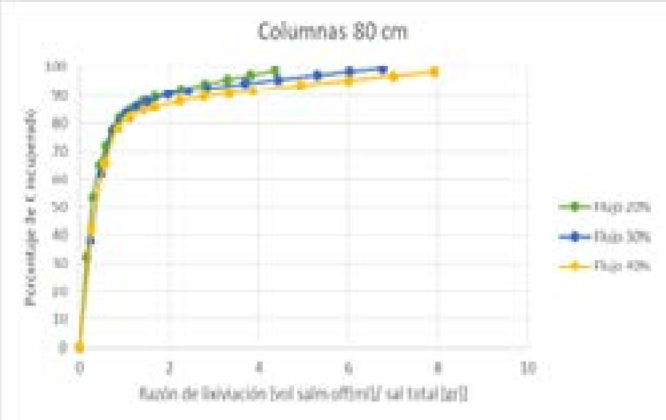

Fig. 8 Comparative graph with height 130 cm and different flow

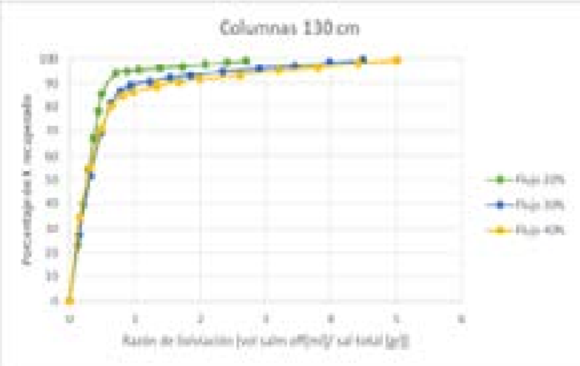

Fig. 9 Graph comparative fico height 180 cm and different flow

4. Conclusions

Experimental results indicate that it is feasible to recover potassium from Halita (NaCl) - Silvita (KCl) preparations with high efficiency and low consumption of brine using the leaching process with a saturated brine in Halita as an extraction route, having a crystal size defined , characterized by sieves of 20% by weight for the # 1/4 mesh sieve, 40% by weight for the # 5 mesh sieve and the other 40% is material retained in the # 100 mesh , at temperatures of the order of 35 at 40 ° C and potassium grade in Halita salt of 7% by weight, formed from a mixture of analytical grade KCl salts and technical grade Halita. The concentration of K in brine recovered after leaching, is measured using selective potassium electrodes (K +), which are calibrated with specific solutions so that these results are tabulated for the 12 columns studied, recording the time observed in each measurement and the volume obtained for each time interval. Errors are estimated at around 15% in these experimental observations.

The most favorable case is when operating with the highest salt height in the column (1.8 m) and at the lowest flow (2.4 l/h), obtaining recoveries around 95% by weight of potassium.

The worst results are obtained in the smaller column (0.5 m) and with greater irrigation flow (4.8 l/h), obtaining recoveries close to 80% by weight of K. The above is explained because achieves a longer residence time of the brine in the salt-filled column. The high yields in all cases are explained since the exchange kinetics between Na+ and K+ is high when compared to copper leaching, high enough to explain yields on an 80% recovery of K in all cases, even in columns of low height and high irrigation rate. It should be noted that the irrigation rates used are high when compared with copper leaching that is around 4 to 50 lt/hr/m2 while in this study irrigation rates of the order of 1333 to 2400 lt/hr/m2.

Additionally, it is observed that the recovery decreases to lower salt heights while increasing otherwise, being its highest value at the height of 1.8 meters where the experimental optimum is obtained in this study. Additionally, the best recovery is at lower leaching rates. It can be concluded that residence time is one of the success factors of having a high recovery that is determined by height and irrigation rate. Obviously the kinetics of exchange between the Na+ and K+ ions is very fast, which explains that at irrigation rates 300 times higher than the case of copper, there are good potassium recovery efficiencies. In addition, it should be mentioned that they are non-porous salts and of granulometry less than copper, which obviously affects these results as observed.

Finally, it should be noted that the graph shows gradualness between the most auspicious result (best recovery) and the one with the lowest recovery, in terms of height and irrigation rate. This is observed by simple inspection of the graphs.

5. Discussions

The results show that the case of higher column height and lower irrigation rate is favorable. It is possible that an optimum can be found at a greater height by decreasing the irrigation rate so as to obtain a high concentration LPS (saturated in K) that recovers the maximum potassium from the loaded column. It is proposed to carry out this study in future research. The latter, however, its importance is not the objective of preliminary study with reference to the properties of these materials and the associated techniques. However, this exploratory study is quite illustrative and will serve as a basis for more rigorous studies with broad access to instruments in the state of the art of technology.

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