

High Purity NaCl from Tailings of Different Mineral Treatments

Antonio Vitellaro and Francesco Lanzino

Italkali S.p.A. Società Italiana Sali Alcalini, Italy

ABSTRACT

In nature, all potassium-containing materials normally also contain quantities of sodium chloride and inerts that must be removed before the industrial use of potassium minerals. To this end, a flotation separation process whose residue, known as flotation tailings, contains nearly all the sodium chloride and inerts, is used. The tailings are not used in industry, because for a successive conversion process, a sodium chloride purity at least 99.4% is required. The general tendency is to discard them as an undesirable by-product. A process by which the sodium chloride of the flotation tailings can be used for industrial purposes is presented in this paper. The process achieves the goal of recovering sodium chloride of sufficiently high purity from the tailings in an essentially simple and direct manner that makes it economically advantageous. Moreover a high yield is obtained and the minimization of the effluent liquids is achieved. The process comprises the following stages: (a) washing the tailings with water and mother liquor from successive stages, to give a mixture whose solid phase comprises nearly all the sodium chloride; (b) separation of this mixture in two turbid portions (hereafter called A and B), the first enriched in solid phase, and the second in liquid phase; (c) separation of A in a solid phase and in part of the mother liquor of stage (a); (d) drying the solid phase of stage (c); (e) recovering from B at least part of the liquid phase constituting part of the mother liquor of stage (a).

INTRODUCTION

In nature, all potassium-containing minerals normally also contain quantities of sodium chloride and clays, which must be removed in order to obtain materials suitable for industrial use. One of the most frequently used processes for this purpose is the flotation process, which consists of treating the minerals (ground and milled to the proper size distribution) with a specific reagent, in a liquid medium, to obtain a product enriched in potassium-containing mineral, and a solid waste (named flotation tailing) containing almost all the NaCl, and small quantities of clays and potassium mineral.

Until now, the flotation tailings have not been used for industrial purposes which require sodium chloride having an NaCl content not less than 99.4%, due to the presence of impurities such as potassium mineral, clays and residual flotation mother liquor and to the very high costs of purification. Hence the general tendency has been so far to discharge such flotation tailings as undesirable waste material. The treatment of these tailings will result in additional cost for industry.

The process described in this paper aims to make the NaCl contained in the flotation tailings from

treating alkaline and alkaline-earth minerals, having an high sulphate level such as kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 2.75 \text{H}_2\text{O}$), suitable for industrial use, recovering it at a purity not less than 99% at a convenient cost. Moreover this process has the advantage of being simple and direct, having an high NaCl yield and, for this, it is applicable in all cases in which the recovery of sodium chloride from flotation tailings is required.

DESCRIPTION OF THE PROCESS

A typical tailing from the flotation process of a potassium mineral such as kainite has an NaCl content not more than 80% w/w, on wet basis, while the remaining components are: kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 2.75 \text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$); schoenite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$); CaSO_4 ; MgSO_4 ; MgCl_2 ; KCl; H_2O ; and clays.

Part of these impurities (kainite, kieserite, calcium sulphate and clays) comes from the raw kainite; the schoenite is formed during the flotation process, and the others (KCl, MgCl_2 , and MgSO_4) are salts dissolved in the flotation mother liquor adhering to the tailings. Therefore the process consists of a combination of selective dissolution stages to elim-

inate the water-soluble impurities, and grading stages to eliminate mainly the clays which are concentrated on the finest particles of the tailing.

Because of the fact that all these impurities are partly segregated in NaCl crystals aggregation, or partly occluded into the NaCl crystals, or partly on the NaCl crystals' surface (i.e. the salts dissolved in flotation mother liquor) the releasing of the segregated/occluded impurities is necessary. This is obtained by destroying the crystals' agglomerates and reducing the tailing size distribution. This reduction of tailing size allows the releasing of impurities, but, on the other hand, increases the NaCl dissolution rate in the washing solution. The dissolution rate of the NaCl in water is higher than that of sulphate but, operating in "almost" saturation NaCl conditions, we are able to considerably reduce this dissolution rate.

Purifying the NaCl contained in the flotation tailing is realized by suspending the tailing in an NaCl solution, having an NaCl concentration of about 20% w/w, containing the water quantity necessary for dissolving the soluble impurities of the tailing. This water has to be metered in order to dissolve the lowest amount of NaCl and to come out from the washing stage with a final solution unsaturated as regards to the magnesium salt having the lowest solubility ($MgSO_4$) in order to achieve its total dissolution.

According to the elaborated circuit the final solution could be fully recycled to the head of the washing stage after adding the proper quantity of water, but to keep the level of impurities in the circulating solution constant, it is necessary to drain a small amount of it. Therefore the process is as follows:

- Reaction between the flotation tailing and an "almost" saturated NaCl solution;
- Hydrocycloning the obtained suspension to remove the clays;
- Centrifugation of the underflow of the hydrocyclone from the previous step;
- Drying the solid phase;
- Mixing brines obtained as overflow of the hydrocyclone and as filtrate of the centrifuge;
- Clarifying the mixture and discharging a part of it;
- Adding water and recycling the brine to the reaction.

Another way that allows better control of the process and its adaptation to specific industrial needs is to realize a double-step washing: the first in which the greatest part of impurities are removed; the second in which the removal of impurities is complete.

The first washing stage substantially has the aim

of destroying the crystals aggregations, releasing the clays and making suitable for dissolution the segregated/occluded impurities. In this step the removal of the greatest part of the impurities occurs and it is possible to eliminate the clays through the grading of the suspension from this first washing stage. In these conditions we have a very low loss of NaCl by dissolution and a solid phase having an NaCl content of 99.0% w/w on dry basis is obtained.

In the second washing step, almost complete removal of the residual impurities is obtained. The limit to total removal of the impurities is constituted by those impurities which remain occluded in NaCl crystals having the largest size and therefore it is not possible, using this method, to reach an NaCl purity higher than 99.5–99.7% w/w, holding an high NaCl yield. Operating in the selected conditions it is possible to obtain an NaCl yield of about 83%, as mass percentage of NaCl treated, with a final product having an NaCl content not less than 99.5%.

THE INDUSTRIAL CIRCUIT

Figure 1 shows a block diagram representing the fundamental units of the industrial circuit. The re-storation brine is prepared by dissolving, with proper reaction water, the finest particles of NaCl which have escaped to the hydrocyclone and centrifuge sections.

First washing step

1. Reaction of the flotation tailing with a solution from the first phase of dissolution of the NaCl finest particles.
2. Hydrocycloning of the suspension from the reaction. The overflow, which contains the greatest part of clays and a certain amount of NaCl finest particles, is fed to a clarifier. The underflow is fed to a first centrifuging section.
3. Centrifuging of the underflow from section 1.2. The filtrate of the centrifuge is fed to the first phase of the NaCl finest particles dissolution. The cake of the centrifuge is fed to the second washing step.

Second Washing Step

1. Reaction of solid phase from section 1.3 with a solution from the second phase of NaCl finest particles dissolution.
2. Hydrocycloning of the suspension from the reaction. The overflow, which contains a certain amount of NaCl finest particles, is fed to second NaCl finest particles dissolution. The underflow is fed to a second centrifuging section.
3. Centrifuging of the underflow from section 2.2.

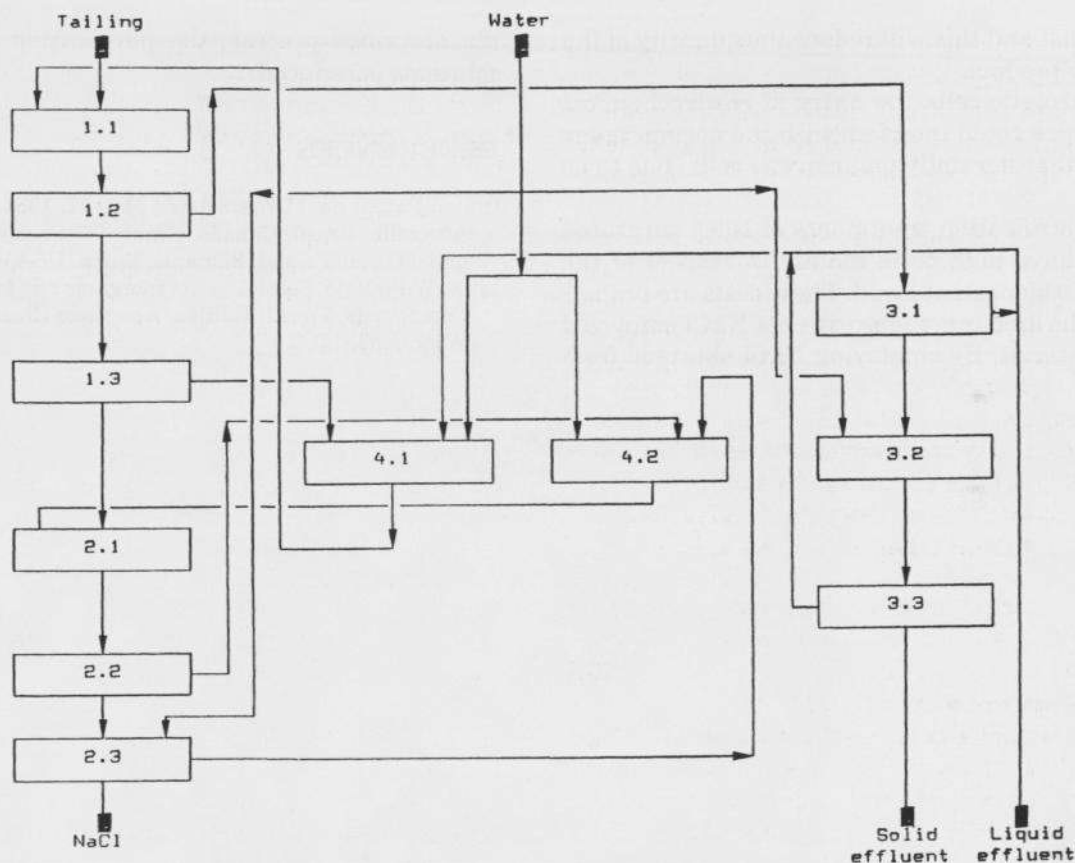


Fig. 1. Block diagram of the double-step circuit for washing kainite flotation tailings.

The filtrate of the centrifuge is fed to the second phase of NaCl finest particles dissolution. The cake is washed with water to remove the adhering solution and is then fed to the drying section.

Clarifying the brines and recovery of NaCl finest particles from the clays

1. The brine from section 1.2 is fed to a clarifier for thickening of the suspended solid (clays and NaCl). Part of the overflow of the clarifier is the liquid effluent of the plant, the remaining part is fed to the first phase of NaCl finest particles dissolution. The underflow, constituted from clays and NaCl finest particles, is fed to the clay washing section.

2. In the clay washing section the underflow from section 3.1 is dissolved by water in order to remove the NaCl fraction. The slurry is fed to a second clarifier.

3. The slurry from section 3.2 is fed to a clarifier. The underflow, constituted by clays and traces of NaCl, is the solid effluent of the plant. The overflow is fed to the first phase of NaCl finest particles dissolution.

Dissolution of NaCl finest particles

The dissolution of NaCl finest particles is realized in two distinct sections in order to keep the brines having different level of impurities separated.

1. The first dissolution section receives the brines from sections 1.3, 3.1 and 3.3 with the proper amount of water. The resulting solution is fed to section 1.1.

2. The second dissolution section receives the brines from sections 2.1 and 2.3, with the proper amount of water. The resulting solution is fed to section 2.1.

CONCLUSIONS

Sodium chloride obtained by the process described can be used in all cases in which it is necessary to prepare an NaCl saturated solution for further use. Before use, these solutions need preventive purification to eliminate the impurities (mainly Ca^{2+} , Mg^{2+} and SO_4^{2-}) which could otherwise not allow, or could restrict, the full use of such solutions. For instance, in a vacuum crystallizer, a high SO_4^{2-} and Mg^{2+} concentration limits the amount of water which can be evaporated before deterioration of the quality of the

final product and this will reduce the quantity of the obtainable product.

In electrolytic cells the entry of electrochemical species which could interfere with the normal redox reactions that normally occur in the cells, has to be avoided.

These purification treatments of NaCl saturated solutions have high costs mainly in respect of the chemical reagents employed. These costs are proportional to the amount of impurities of NaCl employed as raw material. By employing NaCl obtained from

the described process, the purification cost of the solutions is reduced.

REFERENCES

- Italian Patent no. 1157938 dated May 11, 1982. Extended to Australia, Brasil, Canada, France, Germany, Japan, Jordan, Mexico, Poland, Romania, Spain, USA, USSR.
- Linke W.F., 1965. Solubilities of Inorganic and Metal-Organic Compounds, Fourth Edition. American Chemical Society, Washington, D.C.