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Production of Low Bromine-Containing Evaporated Salt

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ABSTRACT

In a purification process for brine, impurities such as Ca^{2+}, Mg^{2+} and SO_4^{2-} are precipitated by the addition of calcium hydroxide ($Ca(OH)_2$) and sodium carbonate (Na_2CO_3). Following NaCl crystallization by evaporation of the brine, a mother liquor is obtained which still contains among others SO_4^{2-}, K^+ and Br^-. Further concentration of this mother liquor by evaporation results in the precipitation of both NaCl and Na_2SO_4 and a more strongly concentrated mother liquor with respect to both K^+ and Br^- remains. This concentrated mother liquor is drained off. Either the precipitated NaCl and Na_2SO_4 are dissolved in water or the Na_2SO_4 is dissolved in brine and then returned to the brine purification process, thereby lowering both the K^+ and Br^- levels in the purified brine. As a consequence the contents of both K^+ and Br^- of the NaCl are reduced.

INTRODUCTION

A large portion of the vacuum evaporated salt produced by Akzo in Europe is used in the chemical industry as a feedstock for conversion into caustic soda and chlorine.

Because of its high purity with respect to Ca^{2+}, Mg^{2+} and SO_4^{2-}, among others, the customer's operating cost shows a good economy in comparison with the use of rock salt for instance. Vacuum salt will show a still better economy when the current trend to put more emphasis on minimizing purge streams develops further as, for environmental reasons, penalties are imposed for the disposal of these streams in general and sludges in particular.

Until now hardly any attention has been paid to the presence in the salt of other compounds like K^+ and Br^-. In an electrolysis plant they end up in the products as KOH and Br_2.

Because in some Cl_2 using processes, i.e. the production of refrigerant 22, bromine has a detrimental effect on either the operating cost or the product quality, prior removal of bromine from chlorine is sometimes required. Although this can be effected in an electrolysis plant, it creates a new environmental problem: how to get rid of the bromine. Such problems facing the salt-using industry can be dealt with by the vacuum salt supplier in lowering the salt's Br content. A method to achieve this purpose is presented.

THE FEEDSTOCK FOR MAKING VACUUM SALT

Crude brine is formed by dissolving NaCl from rock salt in water, which mostly takes place in underground cavities. Salt is produced from the brine by an appropriate treatment followed by evaporative crystallization.

Next to NaCl, the major constituent of rock salt is calcium sulfate which appears in the crude brine as Ca^{2+} and SO_4^{2-} ions in more or less equivalent amounts in general. Next to these can be found varying contents of quite a number of other ions such as Mg^{2+}, K^+ and Br^-. While the occurrence of Mg^{2+} and K^+ is the result of dissolving their respective salts, the source of Br^- is different. As has been pointed out for instance by Raup (1966) the presence of bromine in rock salt has to be attributed to a solid solution as a replacement of chlorine in chloride minerals. In other words, Br^- ions are built into the crystal lattice of NaCl thereby taking the position of Cl^- ions. To what extent this happens is governed by a distribution coefficient having a value of about 0.14 wt.% Br (mineral)/wt.% Br (solution) at the outset of NaCl crystallizing from evaporating seawater (Schneider and Herrmann, 1980). At this particular point the Br content of seawater has risen to about 500 ppm, so the first crystals contain about 70 ppm of Br. As concentration increases further, the Br content of the NaCl climbs to 270 ppm (Raup, 1966). Because of

TABLE 1

Crude brine originating from four sites in north-western Europe

	Site no.			
	1	2	3	4
SO_4^{2-} (meq/l)	60	105	90	55
Ca^{2+} (meq/l)	60	65	80	55
Mg^{2+} (meq/l)	7	22	6	1
K^+ (meq/l)	4	22	6	1
Br^- (mg/l)	30	60	20	50

disturbances during or after the evaporation process such as dilution or recrystallization, the actual Br content of salt rocks shows a much wider range. Figures have been reported of 40–90 ppm (Holser, 1966) and 80–350 ppm (Raup, 1966), which means that one could expect crude brine to contain 10–110 mg/l of Br next to 310 g/l of NaCl.

Table 1 shows the compositions of crude brines originating from several sites in north-western Europe. On the basis of these data, the following composition is used to numerically exemplify the process and its modifications. In order not to obscure the issue, Mg^{2+} and K^+ are omitted.

Composition of crude brine:
NaCl = 310 g/l
SO_4^{2-} = 80 meq/l
Ca^{2+} = 80 meq/l
Br^- = 50 mg/l

THE PROCESS OF MAKING VACUUM SALT

The process is carried through two steps, viz. brine treatment, and brine evaporation and NaCl crystallization.

Referring to Fig. 1, brine is treated prior to evaporation by adding soda ash to precipitate Ca^{2+} in the form of $CaCO_3$. During the evaporation SO_4^{2-} is concentrated close to the solubility of Na_2SO_4. The remaining mother liquor is purged.

At the lowest temperature occurring in a multiple-effect evaporation plant, which is commonly is about 50°C, solubility of Na_2SO_4 is at its highest, viz. 950 meq/l of SO_4^{2-}. By applying a concentration factor of 11.5, the mother liquor contains 11.5×80 = 920 meq/l of SO_4^{2-} and the crude brine required to obtain 1 t of salt amounts to: 11.5/ (10.5×0.31) = 3.533 m^3. Taking into account an excess of CO_3^{2-} in the purified brine equal to 10 meq/l, soda ash requirement is (80 + 10) × 3.533 × 0.053 = 16.85 kg/t of salt.

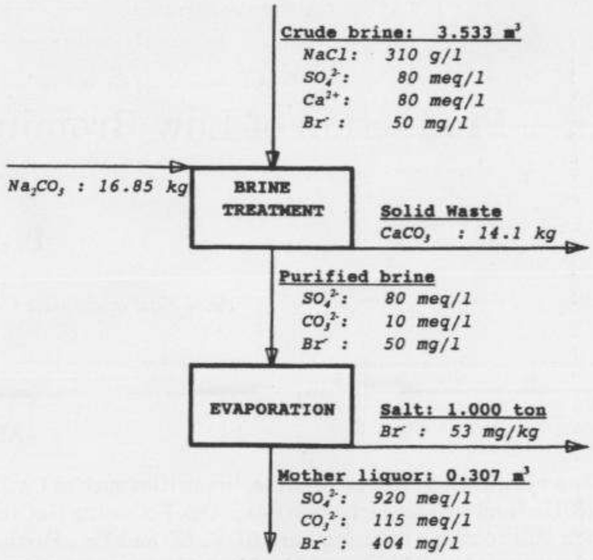

Fig. 1. Vacuum salt plant with one-stage brine treatment.

Results of these mass balance calculations have been summarized in the block diagram in Fig. 1.

Superimposing a bromine balance, Br contents of both salt produced and mother liquor are found to be 53 mg/kg and 404 mg/l respectively, based upon an average distribution coefficient of 0.13 mg/kg (salt)/mg/l (solution) being equal to about 0.16 wt.% (salt)/wt.% (solution).

This coefficient has been repeatedly confirmed in Akzo's plants. It depends somewhat on temperature and is slightly in excess of the seawater figure, while it agrees neatly with the coefficient valid for the system Na^+–Cl^-–Br^-–H_2O (Braitsch, 1962, Abb. 32). One will note that 30% of the bromine entering the process ends up in the product.

For the sake of completeness it is mentioned that minor details such as the brine which is disposed of together with the precipitates and the liquid adhering to the salt crystals were left out of the mass balance.

A COST EFFECTIVE TREATMENT

As has been described in a German patent already 90 years ago the Swiss salt producers at Schweizer-Halle found an elegant method of substantially reducing the cost of treating the brine by creating such conditions that Ca^{2+} is removed as gypsum, thereby using SO_4^{2-} present in the crude brine.

Returning sulfate-rich mother liquor to the purification, a mixture is obtained the $CaSO_4$ ionic product of which exceeds the solubility product of about 9,000 (meq/l)^2 and in consequence gypsum is precipitated according to:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O\downarrow \qquad (1)$$

After equilibrium has been attained the Ca^{2+} ions left over are precipitated in a next stage by using soda ash again.

The treatment is further improved by adding lime to the first stage, thereby replacing SO_4^{2-} by OH^- according to:

$$Ca(OH)_2 + SO_4^{2-} + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O\downarrow + 2OH^- \qquad (2)$$

By injection of flue gas in the second stage OH^- in its turn is converted with CO_2 into CO_3^{2-}:

$$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \qquad (3)$$

The CO_3^{2-} ions thus obtained serve to precipitate Ca^{2+}, of course. Combining reaction equations (2) and (3) the overall effect can be described as making a more expensive chemical compound, i.e. soda ash, from a cheap commodity, i.e. lime:

$$Ca(OH)_2 + SO_4^{2-} + H_2O + CO_2 \rightarrow CaSO_4{\cdot}2H_2O\downarrow + CO_3^{2-} \qquad (4)$$

Because of the rather limited solubility of lime in brine, the operation cannot be pushed to its extreme where no additional soda ash is required at all, which means that in the case under consideration a small amount of SO_4^{2-} has still to be purged.

An example of a salt plant incorporating such a two-stage brine purification is shown in Fig. 2. Its cost effectiveness is represented by the low soda ash consumption of 2.48 kg/t of salt.

By again superimposing the bromine balance the outcome is an increase of the salt's Br content to 119 mg/kg, because the overall concentration factor has risen to 3.275/0.049 = 67. The product contains 73% of the bromine entered with the crude brine.

LOWERING THE BROMINE CONTENT

In order to lower the Br content, the obvious solution is to reduce the overall concentration factor by enlarging the mother liquor purge. However, in so doing, more SO_4^{2-} will get lost which must be compensated for by a rise in soda ash consumption.

Ultimately one could end up with a kind of operation as shown in Fig. 1. Both to prevent this drawback as well as to redress the outcome as presented in Fig. 2, a way of operation is aimed at whereby the purge is kept more or less the same, while its Br content is much higher.

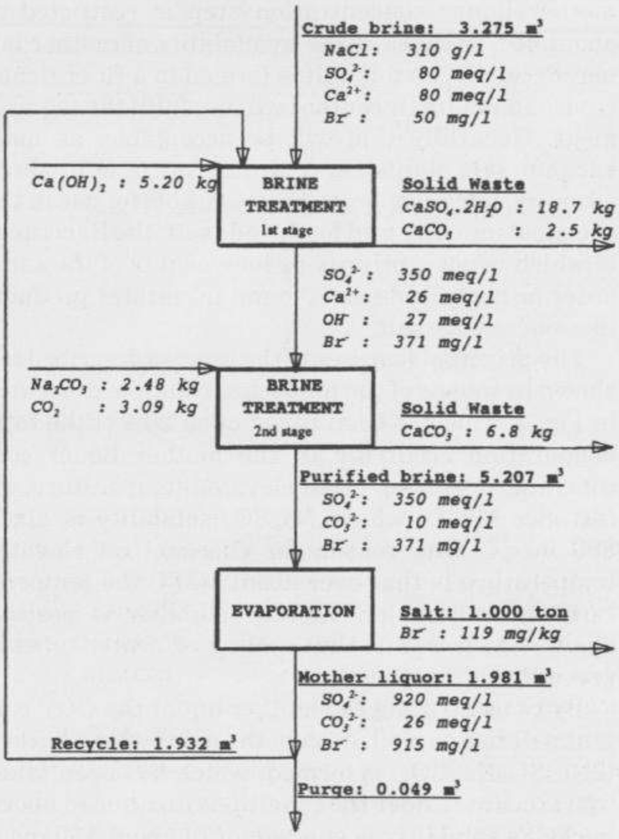

Fig. 2. Vacuum salt plant with two-stage brine treatment.

As has been explained before, the evaporation of brine is stopped just prior to attaining the solubility limit of Na_2SO_4. Crossing this threshold, however, will result in simultaneously crystallizing NaCl and Na_2SO_4 and concentrating the soluble compounds like Br in the liquor. By discarding the concentrated mother liquor, the Br outlet from the process is shifted from salt to liquid purge which is what was aimed at.

In order to retain the benefits of precipitating gypsum in treating the brine, a way has to be found for reintroducing the crystallized Na_2SO_4 into the brine cycle. Dissolving the crystal mix obtained in the mother liquor concentrator in water is, indeed, self-evident but it will not be dealt with because of its adverse effect on the energy cost.

By reslurrying the crystal mix in purified brine in such a ratio that the resulting SO_4^{2-} content approaches the Na_2SO_4 solubility and returning the sulfate-enriched brine to the treatment, the cycle becomes closed again. As the brine is already nearly saturated with respect to NaCl, solid NaCl remains virtually unchanged and is separated from the liquid.

Two aspects must be pointed out. Firstly the fraction of total salt production crystallized in the mother liquor concentration step is restricted to about 40% because of the availability of mother liquor. Secondly, as this salt is formed in a Br enriched environment its Br content will not fulfil the requirement. Generally this will be acceptable, as most vacuum salt plants serve a dual purpose productwise, viz. pure evaporated salt suitable for use in the chemical industry and food grade salt, the Br content of which is not a priority as long as it is of the same order or magnitude as is found in natural products like sea or rock salt.

The principal features of the process described are shown by means of the numerical example presented in Fig. 3. This has been based upon 20% of the total evaporation occurring in the mother liquor concentrator operating at an elevated temperature, for instance 120°C, where Na_2SO_4 solubility is about 800 meq/l. One reason for choosing an elevated temperature is that over about 100°C the temperature dependence of Na_2SO_4 solubility is positive again, which means that scaling of heater tubes is prevented altogether.

By concentrating the mother liquor the CO_3^{2-} content will rise as well, even to the point where burkeit ($2Na_2SO_4Na_2CO_3$) is formed, which has been taken into account. Under the conditions mentioned above, burkeit's solubility is equivalent to about 150 meq/l of CO_3^{2-}.

When comparing Fig. 3 with Fig. 2, the substantial reduction of the Br levels in the process liquors and the Br content of the major part of the product can immediately be seen. A closer inspection reveals that in this in this case $(0.8 \times 27 + 0.2 \times 249)/(3.275 \times 50) = 43\%$ of the bromine entering the process leaves with the products.

REMOVAL OF POTASSIUM

Potassium behaves like Br; it is also built into the NaCl crystal lattice, although its distribution coefficient is much lower. In those instances where customers demand a lower K^+ content of the salt this can be met by further concentrating the mother liquor, thereby decreasing all K^+ levels as well.

ANOTHER OPTION FOR THE REMOVAL OF BROMINE

A quite different method for reducing Br^- levels throughout the process is oxidation of Br^- to BrO_3^-. Because bromate ions are not accepted in the NaCl crystal lattice, the NaCl's bromine content will become very low. However, in consideration of the fact that BrO_3^- ions are unstable at elevated temperatures and will act as an oxidizing agent for commonly used construction materials in the evaporation plant such as CuNi 70/30 and Monel 400, the possible attractiveness of this method disappears completely.

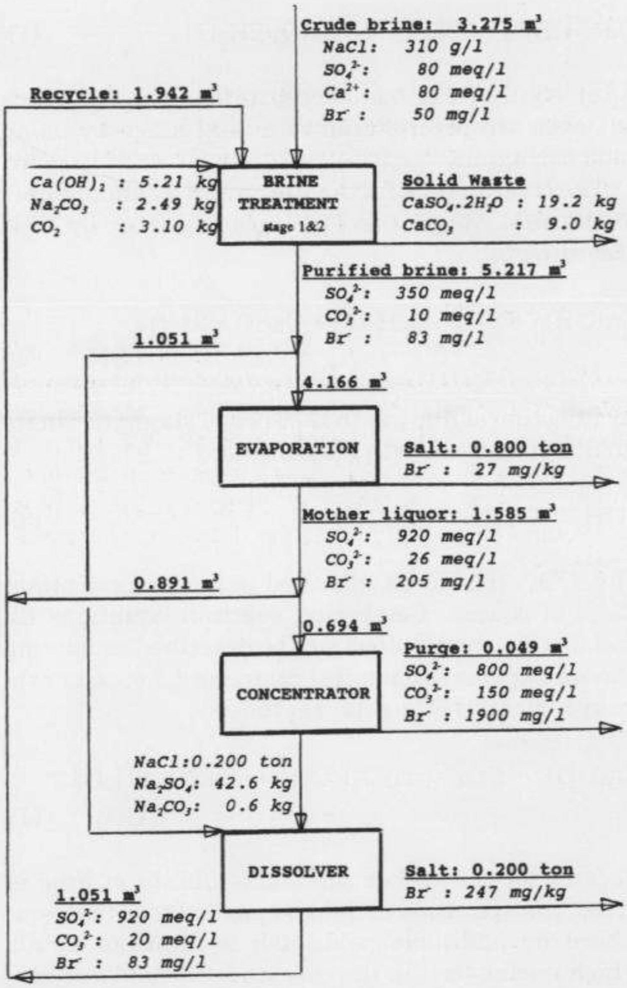

Fig. 3. Vacuum salt plant with two-stage brine treatment and mother liquor concentrator.

Another argument which can be used against employing a method like this one is that the levels of other ions, like K^+, remain unaffected.

EXPERIMENTAL WORK

The simultaneous crystallization of NaCl and Na_2SO_4 from the mother liquor has been tested at the pilot plant scale. It was found that the Na_2SO_4 crystals obtained are of about the same size as the NaCl crystals, viz. about 350 μm on average.

Batchwise experiments carried out at the laboratory scale indicate that dissolving Na_2SO_4 in brine again occurs fairly rapidly. Up to 10 min is sufficient to complete it.

FULL SCALE PRACTICE

Currently Akzo is in the process of changing its operation at the Hengelo salt works by re-arranging the feed and discharge lines to and from one of the evaporators and by installing Na_2SO_4 dissolving equipment. Full scale results cannot therefore be reported yet.

CONCLUSION

When addressing the requirement to lessen Br^- and/or K^+ content of pure vacuum salt, this can be met by further concentrating the mother liquor and re-dissolving the Na_2SO_4 thus obtained in brine. In doing so the benefits of a brine treatment based upon the precipitation of gypsum are not lost. A patent has been applied for.

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