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STUDY ON DECANTATION WAYS OF ROCK SALT BRINES AND THEIR EFFECTIVE USE

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Abstract

Rock salt from Dhrovjani mine (Delvina) is characterized by a very high content of insoluble in water matter (around 20%). Nevertheless, it has been used for more than 20 years in some industrial areas, particularly in soda ash production at the Vlora plant. The use of this kind of salt is accompanied by large amount generation of solid waste, and also by limited decantation rate of raw brines prepared, in particular during the wet seasons (when the salt moisture content exceeds 2.5%). The study was undertaken in relation to this rocky salt, as well as to the possibility of decantation rate increasing of the crude brines.

Key words: Decantation, coagulation, rock salt, brine, Dhrovjan (Delvina).

1. Introduction

In Albania is traditionally produced sea salt, and rock salt production began for the first time in 1970 [1], with the operation of the mine of Dhrovjan (Delvina – South Albania). This salt was used mainly as a raw material for the production of calcinated sodium plant in Vlora. Deposit reserves are estimated at billion of tons, and are characterized by a wide range and a depth typically of 20-50 m, but it can reach up to 1000 m.

The difficulty of using this salt is not only to the high content of substances insoluble in water, but in very small speed decantation of crude brine (separation of solid materials from the brine solution) in the wet seasons of the year. The natural moisture of ore extracted from mines (usually up to 2%) does not have any negative impact on the process of brine decantation; on the contrary, when the salt is washed by atmospheric precipitations during production, storage and transportation of it, then there are noticed serious difficulties in the process of producing pure brine solution, in order to meet quality requirements in the production of sodium, etc [3]. The overcoming of these difficulties has been achieved through the use of flocculants (poliacrilamid, separan) in the decantation process [7]. But the goal is to find other effective solutions that are simpler and less expensive.

In order to stabilize the solid particles in water and to increase the velocity of their sedimentation, there are used coagulant materials. The technical literature suggests in a wide use the aluminum sulphate $Al_2(SO_4)_3$, as well as iron sulphate $FeS0_4$ [2, 5]. After the addition of aluminum and iron salts in water, they dissolve, hydrolyze and polymerize, forming coagulant products, which are very effective due to the fact that there takes place the absorption of complex metallic ions on the surface of negatively charged solid particles.

2. Materials and Method

2.1. Preparation of brine in laboratory conditions

This preparation it was conducted in a special salt solver, which construction and functioning was similar to that used in industrial conditions.

This 300 mm height cylindrical equipment works according to the principle of opposite currents, where water enters from below and pierces the rock salt layer, which is given from above, in amounts accordingly to its solution. In the middle of the device (in height 150 mm) there is a circular ring with external diameter of 100 mm (equal to the internal diameter of the solver) and internal diameter of 50 mm, the function of which is avoiding short roads, aiming to ensure a better contact between salt and water.

At the upper part of the solver, in the height of 270 mm, there is situated a circular outer ring, where the prepared brine is overflowed and then taken off. Samples of raw material is broken and finely crushed to the extent <0.2 mm. In order to ensure uniform composition of brines, the first portions are flowed away, while the preservation of the prepared brines is carried out in containers equipped with agitators.

Decantation speed survey was conducted in the brine graduated cylinders. In determining the speed of decantation in the laboratory we used the notion of the “sedimentation rate”, which expresses the percentage ratio between the volume occupied by sediment, after complete separation of phases,(during the time of 1 hour accepted to complete decantation), versus the full volume of suspension. The average decantation speed for these conditions is calculated in cm/hour.

2.2. Definition of chemical composition of the rock salt of Dhrovjan

There were taken seven samples and for every sample it was defined by chemical analysis [10], the concentration in g/l of insoluble matter, $CaS0_{4,}$ $MgCl_{2,}$ NaCl and moisture.

2.3. Definition of chemical composition of brines obtained in industrial conditions and their decantation velocity.

Chemical analysis were performed on seven samples of brines obtained in industrial conditions according to [10]. In this way there were defined the concentration of NaCl, MgO, CaO and moisture content, in a temperature of $24^{o}C$. It was defined as well, the decantation velocity in cm/hour [7].

2.4. Laboratory study on the effect of temperature on decantation parameters

There were defined the key parameters of decantation such as: sedimentation volume(%), decantation velocity (cm/hour) and velocity increasing rate(%), [6] in five samples, with an increasing order of 10^oC, starting from 30^oC and ending at 70^oC, holding a constant concentration of 313,4 g/l.

2.5. Study of $FeS0_4$ impact as a coagulant in the decantation of rock salt brine

For this purpose there were carried out tests, using as a coagulant $FeSO_4$. The coagulant was prepared as a solution of pure FeS04 in 500 ml of water. In these trials it was used brine obtained from rock salt moisture content of 3.4%. The trials were realized in six samples with an increasing concentration of $FeS0_4$ solution, from 0,1 g/100 ml brine to 0,2; 0,4; 0,8 and 1,6 g/100 ml brine There were defined the sedimentation volume(%), decantation velocity (cm/hour) and the increasing rate of velocity(%) [5].

2.6. *Study of $(Al)_2(S0_4)_3$ impact as a coagulant in the decantation of rock salt brine*

The coagulant was prepared dissolving 40 g of $Al_2(SO_4)_3$ in 500 ml water. In these trials it was used brine obtained from rock salt moisture content of 3.4%. The trials were realized in six samples with an increasing concentration of $(Al)_2(S0_4)_3$ solution, from 0,1 g/100 ml brine to 0,2; 0,4; 0,8 and 1,6 g/100 ml brine There were defined the sedimentation volume(%), decantation velocity (cm/hour) and the increasing rate of velocity(%) [5].

3. Results and discussion

Rock salt of Dhrovjan has a microcrystalline structure. The content of its main components is givenin Table 1. Negative indicator of the quality of this salt, which hinders its usage, is the high content of substances insoluble in water (18,04 - 19,36%), while as a positive quality, especially in Soda production industry, is the low content of magnesium salts, expressed as $MgCl_2$. This content fluctuates in the range of 0,33% and 0,57%. This fact does not occur in the sea salt, where $MgCl_2$ content is found to be more than 1%. Natural moisture is less than 2%, and values above this limit are always connected to the effect of atmospheric precipitations in the process of extraction, storage and transport of rock salt. This fact has serious consequences during the industrial use of rock salt, since they limit significantly the decantation velocity of crude brines (in a suspension state), which are produced in industrial conditions.

Regarding the composition of the brine (Table2), it is observed a very low content of magnesium salts (expressed as MgO) versus the content of calcium salts, expressed as CaO [10]. It is noted also that the decantation velocity of brines obtained from salt rock with high moisture content due to atmospheric precipitation (6,02%), decreases more than three times compared to the velocity of decantation of salt brine obtained with normal humidity content (1,86%).

Table 1: Chemical composition of Dhrovjan Salt (mass %)

Sample nr.	*Insoluble matter*	*$CaSO_4$*	*$MgCl_2$*	*NaCl*	**Moisture**
1	19.07	3.61	0.35	74.92	1.99
2	18.43	3.62	0.35	76.02	1.44
3	19.56	9.67	0.33	75.09	1.40
4	19.36	3.82	0.42	75.41	0.96
5	18.04	3.85	0.47	76.20	1.08
6	18.06	3.67	0.35	76.10	1.86
7	18.37	3.77	0.38	75.32	2.08
8	18.74	3.70	0.37	75.40	1.71
9	18.98	3.70	0.47	74.81	1.91
10	18.65	3.77	0.57	74.85	1.16

Table 2: Chemical composition of brines obtained in industrial conditions and decantation velocity.

Sample nr.	*Concentration g/l*			*Temperature*	*Salt Moisture*	**Decantation**
	NaCl	CaO	MgO	*^oC*	*%*	**velocity cm/hour**
1	314,4	2,45	0,10	24	1,86	8,4
2	313,3	2,38	0,10	22	1,36	8,8
3	314,2	2,4	0,10	24	6,02	2,8
4	314,5	2,45	0,11	24	5,50	3,2
5	314,0	2,38	0,12	23	1,14	8,8
6	314,2	2,24	0,10	24	1,74	8,5
7	314,5	2,24	0,11	24	2,82	6,00
8	314,2	2,43	0,12	24	3,40	5,20

Table 3: Chemical composition of insoluble matter in water (%), referred to 100 g of dry crude salt

Sample nr.	*SiO_2*	*Fe_3O_4*	*SO_4^{2-}*	*CaO*	*MgO*	**Al_2O_3**
1	7.40	1.06	1.38	2.16	1.76	2.98
2	8.73	1.31	2.10	1.91	1.63	3.21
3	7.82	1.28	2.15	2.05	1.68	3.12

Table 3 shows the composition of the insoluble residues in water (referred to 100 g of dry crude salt). Fine fractions below 0.2 mm represent mainly clay material, while fractions larger than 0.2 mm are sulphate calcium and carbonate.

In Table 4, it is presented the influence of temperature on the decantation velocity of brine. It may be seen that there is an increase of the velocity in the amount of 0,5 – 0,7cm/hour, for every rise in temperature with 10^{o}C. To be able to apply this conclusion in industrial conditions it will be necessary the preheating with water steam to be used for the dissolving of the salt, which in terms of production is of interest up to the values of 40-45^{o}C. This preheating is indispensable to speed up the process of salt dissolving in water, while above this temperature – there is no more economical interest.

An effective way to increase the speed of decantation of brine is the use of coagulants. For this purpose there were carried out tests, with coagulants such as $FeSO_4$ and $Al_2(SO4)_3$. In these trials was used brine obtained from rock salt moisture content of 3.4%. Table 5 presents the effect of iron sulphate on the decantation velocity of the brines. Table 6 presents the effect of aluminium sulphate on the decantation velocity of the brines. In Table 6 it is observed that the use of coagulant $Al_2(SO_4)_3$ has a relatively good effect on the decantation velocity, especially in comparison to the use of $FeSO_4$ as a coagulant.

Table 4: Temperature effect on decantation velocity of brines

Sample nr.	*Temperature (^0C)*	*Sedimentation volume (%)*	*Decantation velocity (cm/hour)*	*NaCl (g/l)*	**Velocity increasing rate (%)**
1	30	18.8	8.6	313.4	-
2	40	19.2	9.0	313.3	4.65
3	50	18.5	9.5	313.4	10.46
4	60	19.0	10.1	313.4	17.44
5	70	19.2	10.7	313.2	24.41

Table 5: Coagulant $FeSO_4$ effect on the decantation velocity of brines (in 27°C)

Sample nr.	*Dose, (g/100ml)*	*NaCl (g/l)*	*Sedimentation volume (%)*	*Decantation velocity (cm/hour)*	**Increasing rate of velocity (%)**
1	-	314.5	20.0	5.0	-
2	0.1	314.4	21.1	5.4	8
3	0.2	314.4	20.5	5.7	14
4	0.4	314.5	20.0	6.0	20
5	0.8	314.4	21.0	6.2	24
6	1.6	314.5	20.5	6.4	28

Table 6: Coagulant $Al_2(SO_4)_3$ effect on the decantation velocity of brines (in 27°C)

Sample nr.	*Dose g/100ml*	*NaCl g/l*	*Sedimentation volume %*	*Decantation velocity cm/hour*	**Velocity increasing rate (%)**
1	-	314.5	20.2	5.4	-
2	0.1	314.2	18.8	6.2	14.8
3	0.2	314.5	19.5	7.0	29.6
4	0.4	314.4	18.6	7.7	42.6
5	0.8	314.4	19.0	8.7	61.1
6	1.6	314.5	18.5	9.8	81.5

The content of 2% of moisture in the salt to be used for brine preparation does not limit the decantation velocity of the brines. The increase in moisture content due to atmospheric precipitations decreases with three times the decantation velocity in industrial conditions; in this case it is indispensable the use of flocculants with have high impact on the decantation process.

The increasing of water temperature for salt solution affects positively the decantation velocity of brines, leading to the increasing of their concentration; for economical reasons this temperature should not excess the value of 45^0C. The optimal limit of water temperature during the process of salt solution, is a technological necessity for qualitative production of brines, while the $Al_2(SO_4)_3$ has the best effect between other inorganic coagulants tested.

The main factor bringing to the reduction of the flocculants quantity necessary to be used in the process, is to preserve well the salt, avoiding as much as possible its contact to the atmospheric precipitations. These conditions will bring to a use of only 20 g/ton of processed salt, which has an insignificant impact on the industrial production cost.

Despite the fact that $Al_2(SO_4)_3$ shows best effect among other inorganic coagulants [4], these results are still not acceptable for industrial scale.. In industrial conditions it would be of more interest the use of flocculants with a better effect, such as polyacrilamide and separan, with an average consume of 20 g/ton treated salt [8]. This low quantity of flocculent use it is explained with its limited use – only in the periods when the moisture of salt is higher than 2%, due to atmospheric precipitations. The reduction to a minimum of the salt moisture in the wet seasons of the year, as well as the use of suitable flocculants such as polyacrilamide and separan for speeding up the process of decantation, make possible that the rock salt of Dhrovjan be used for a long time (almost 20 years), as the first raw material for industrial production.

4. Conclusions

- The rock salt of Dhrovjan is characterized from a high content of insoluble matter in water (18-20%), which limits its possibilities of industrial use, due to high amounts of solid production wastes.
- The content of magnesium (expressed as $MgCl_2$) in the rock salt of Dhrovjan is low (0,35-0,57%). It is lower than the content of calcium (expressed as $CaS0_4$), which varies from 3,61-9,67%. The moisture content of the ore hardly exceeds 2% (1,40 – 2,08%).
- The salt brine obtained in industrial conditions results in a low content of magnesium salts (expressed as MgO), averagely 0,1%, while the content of calcium salts(expressed as CaO) is 2,3%.
- The decantation velocity of brines obtained from salt rock with high moisture content due to atmospheric precipitation (6,02%), decreases more than three times compared to the velocity

of decantation of salt brine obtained with normal humidity content (1,86%).

- The decantation velocity of the raw brine increases with 0,5 – 0,7 cm/hour, for each increase of $10^{o}C$ in the temperature of the brine. The preheating of the brine using water vapor above $40\text{-}45^{o}C$ – it is practically proved to be not of economical interest.

- The use of $FeS0_4$ as a coagulant in brine decantation, showed to be of no interest, since the velocity speed was low for all doses of concentration of $FeS0_4$ in the brine (5,4 – 6,4 cm/hour).

- The use of $Al_2(SO_4)_3$ as a coagulant in brine decantation gives better results than the use of $FeS0_4$. The velocity of decantation increase from 5,4 to 9,8 cm/hour.

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