Utilization of building brines in the process of creating underground reservoirs using the method of dissolving in rock salt beds

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At the Astrakhan gas condensate field, the construction of underground reservoirs for holding of oil, natural gas, and products of their processing is carried out. In the course of salt deposit dissolving, associated brines are formed with a concentration from 60.0 to 305 g/l. The problem of subsequent utilisation of those brines is the primary one that should be solved to provide environmental safety and to produce inexpensive sodium chloride necessary for industrial purposes.

For the first time in the world, a method for evaporation of salt brines at ambient temperature in lake-deflation hollows is used at the Astrakhan gas condensate field (GCF). The most suitable regions for free evaporation at ambient temperature are dry areas with a hot climate, a high vaporising ability and a small amount of falls. Astrakhan, Orenburg, Kazakhstan, and Middle Asia are among these areas. The mean values of yearly evaporation (according to data of the Kharabaly station) and that of atmospheric falls in those regions are equal to 1, 100.0 and 215.0 mm, respectively. The evaporation exceeds falls by 850.0 - 900.0 mm/year. The highest temperature in these regions was registered from May to September and the average ambient air temperature for the last 10 years - 9.4 ^{0}C.

In geomorphologic respect, the semidesert and desert regions represent an alternation of elevated parts of land and hollows the depth of which may range from 1 to more than 3m. The bottom of these hollows is pickled with salt and salt deposit areas are visible on the surface. In spring and autumn season the bottom of hollows is covered with a brine layer. Hydrogeological and geophysical inspection have proved the existence and availability of naturally formed concentrated brines due to ground water evaporation when the water horizons are not far from ground surface. On the basis of this fact it was suggested that such hollows could be used for accumulation of brines associated with construction works and for their successive free evaporation.

Two hollows were chosen for pilot operation: the former Karasor and Aidyk Lakes, which had dried up completely to the moment. Hydrogeological inspection was carried out and water and salt balances were calculated to substantiate the environmental and economic expediency of utilisation of associated brines in those hollows. The dried lakes were furnished with surrounding dams, wells for hydrogeological control, and hydrometric posts.

During 7 years, associated brines were released for free evaporation into the dry Aidyk Lake. The resulting salt layer was of 70.0-cm depth and the total weighed around 68.0 tons. Presently, the salt forma tion is developed as a salt production source for the population and the brine from the lake is used for well drilling.

Water from Buzan River is used for dissolving of salt deposit together with preliminary treated wastewaters from the Astrakhan Gas Processing Plant. The chemical composition of these wastewaters is very different: they contain magnesium, calcium salts, chlorides and a variety of other compounds [2].

During free evaporation the brine in the lake cup was exposed to high and low temperatures, atmospheric falls and dominating winds.

After saturation was achieved (317g/1), small crystals of salt were formed at the brine surface that precipitated at the bottom to yield a salt layer. During the whole process of brine evaporation, the brine state in the lake, the hydrochemical regime of the water-bearing horizon, the salt concentration of surface soil and ground in the lake district were monitored. Geophysical methods (VEZ) [3] were applied to look for the movement of the brine filtration front in the water-bearing horizon.

Associated brine is a product prepared by dissolving of salt deposit in water. It is reasonable to assume that the chemical composition of the brine and precipitated salt depends on the solvent and salt deposit composition. Besides, climatic factors such as air temperature, falls and the amount of evaporated water should influence the brine composition in a lake cup.

It was shown by chemical analysis that the average content of sodium chloride in salt deposit from Seitovsky dome of Astrakhan field [4] is 88.19%, whereas that of sulphates is 3.14%, and water insoluble impurities is 5.64%. Some data on the chemical composition of salt deposit from Seitovsky dome of Astrakhan field are given in Table 1.

Table 1. Macrocomponent Composition of Salt deposit from Seitovsky Dome at Astrakhan Field

Ions, compounds	Mean value %
Sodium	34.675
Potassium	0.0225
Calcium	1.3088
Magnesium	0.1468
Chlorine	54.250
Sulphates	3.1370
Carbonates (HCO_3)	0.1828
insoluble residue	5.6401
NaCl	88.1887
Number of analysis (n)	65

The data on microcomponent composition of salt deposit from Seitovsky dome presented in Table 2 show that concentration of such hazardous elements as lead, cadmium, and iron exceeds Acceptable Ceiling Concentration (ACC) by 6.2, 12.3, and 2.4 times, respectively.

Usually, the major part of mountain formations contains mechanical and chemical impurities as well. Salt deposit (evaporated) formations also contain many elements. Thus, manganese is accumulated in gypsum in large quantities whereas iron is kept presumably in solution. Small portions of the latter are included into crystal lattice of evaporated minerals, then removed from those during dissolving process and transferred to the surface together with brine. All salt deposits obtained by evaporation are a large depot of copper, lead, zinc; non-ferrous metals are scattered in the mass [5].

Mineralised waste waters used for dissolving of salt deposit absorb from the mass large amounts of cations and anions.

During this process, sulphates and carbonates of magnesium, calcium, and zinc remain in an underground reservoir as an insoluble residue due to their low solubility in water. This procedure improves brine quality by removing unusable impurities. Besides, in wintertime, when temperature drops , the precipitation of sulphates occurs directly in brine pipelines during brine transport from underground storage sites towards accumulating lakes.

This was supported by the results of laboratory experiments regarding the influence of low temperatures on composition of the formed salts. Table 3 summarises the results of laboratory experiments. The amount of insoluble impurities in brine decreases after freezing from 3.57 w% to trace amounts, the content of calcium and sulphates reduces from 1.93 to 0.05 w% and from 0.74 to 0.18 w%, respectively, whereas the content of sodium chloride NaCl increases accordingly from 93.64 to 99.36 w%.

Table 2. Content of Hazardous Elements in Salt Deposit from Seitovsky Dome at Astrakhan Field

Element	Content of an element in salt deposit, mg/kg	Acceptable Ceiling Concentration (ACC) for Food Salt *), mg/kg	n Fold Exceeding of ACC, times
Pb	12.5	< 2,0	6.25
Cd	1.23	0,1	12.3
Cu	1.6	3.0	-
Zn	1.65	10.0	-
Fe	121.7	50.0	2.4

*) from "Medical and Biological Requirements and Sanitary Norms for Food Materials and Food Products Quality", Official Publishers, GOST 13830-91

Table 4 shows chemical composition of evaporated salt in Aidyk Lake.

For the period from 1991 to 1993 the amount of calcium and magnesium salts decreased from 0.3 to 0.027 and from 0.08 to 0.01 w% respectively and that of sulphates dropped from 1.79 w% to traces. The percentage of insoluble residues decreased by a factor 10: from 2.14 to 0.2 w%.

The role of external factors on the process of self-purification in accumulating lakes is of great importance. Further study of this process would allow applying such morphological structures for utilisation of associated brines for the environmental protection and for production of cheap mineral substance - sodium chloride.

Table 3. Macrocomponent Composition of Original Salt before (1) and after Freezing Procedure (2) (mass %)

Componen t	Samples	
	1	2
NaCl	93.644	99.365
Cl	56.793	60.543
Mg	0.107	0.4
Ca	1.935	0.0491
Insoluble	3.57	traces
Rest	0.744	0.1814
Total	100	100

2. Assessment of the Evaporated Salt from Aidyk Lake

It was found that for almost 7 years of free evaporation of associated brine in Aidyk Lake the evaporated salt layer grew up to 70 cm in depth and a mass of about 68 thousand tons [6].

For quality determination 24 wells to a depth of 0.8 in were drilled. The well drilling has been performed in a way to provide complete pass through the salt layer without touching the bottom dirt. Sampling was made from the whole area around profiles and cuttings. 72 samples have been taken out. These samples were analysed in laboratories to detect macro and microcomponent composition (toxic elements such as Cu, Pb, Cd, Zn, Fe, As, Hg). The original salt is a white, dense substance consisting of middle and large size crystals with well defined sodium chloride crystals. The content of NaCl is 97.56 % at a variation coefficient of 4.328 while amount of insoluble admixtures is 1.139 % at a variation coefficient of 4.189. The major cation components are sodium and potassium, 38.42% by weight. The percentage of magnesium is 0.024%, the amount of sulphates ranges from 0.08 to 1.96% (mean 0.512%) with a variation coefficient of 0.338. The results of analysis of 62 salt samples (10 samples with abnormally high values have not been taken into consideration) were statistically treated to get the reliable results. It was concluded that the mean content of NaCl was 98.376% at a variation index of 0.728 and the mean value for insoluble fractions was 0.420% at a variation index of 0.546. Statistical treatment of macrocomponent composition data of evaporated salt (72 samples)

Table 4. Composition of the Evaporated Salt from Aidyk Lake

Component	Date of sampling				
	June, 1991	Sep.' 1991	June,1992	June,1993	June,1997
Ca	0.345	0.458	0.104	0.027	0.252
Mg	0.084	0.089	0.013	0.011	0.024
Na+K	32.68	37.55	38.86	39.071	38.42
HCO_3	0.421	0.359	0.253	-	-
Cl	49.67	57.376	60.041	60.385	59.28
S04	1.79	1.97	-	traces	0.512
NaCl	81.79	94.48	98.13	99.303	98.376
Insoluble admixtures	2.145	1.365	0.087	0.21	0.420

from Aidyk Lake proved that this salt meets the requirements for food salt of that between first and second grades (NaCl content should be 97.56%). Chemical analysis data of 62 salt samples (excluding 10 non-conditional boundary samples) showed the evaporated salt may be specified as first and highest-class quality product (NaCl content is 98.376%, see Table 5). Assessment of the results of analysis showed that the concentration of toxic elements in evaporated salt did not exceed the norms of "The Requirements to the Quality and Safety of Food Materials and Products", SaNPiN 2.3.2.560-96.

On the basis of the State Expertise performed by the Hygienic Certification Centre for Food Products at the Institute of Nutrition of the Russian Academy of Medical Sciences, the Hygienic Certificate was obtained for the food sodium chloride. The content of hazardous components in a sample of the evaporated salt is as follows:

Lead- 0.179 mg/kg; Mercury -0.009mg/kg; Zinc - 1.27 mg/kg; Cadmium - 0. 107 mg/kg; Copper - 0. 13 1 mg/kg; Arsenic - 0. 168 mg/kg.

The results of analyses regarding radioactivity and benzopyrene content in evaporated salt proved that it was suitable for food consumption (Hygienic Certificate N 72-TSGS-2845 from June 3, 1997),

Evaluation of Salt and Brine Stock

The evaluation of salt and brine reserves in Aidyk Lake were described in "The scheme of distribution of various brands of evaporated salt in Aidyk Lake", "The scheme of isoconcentration depths", "The scheme of isopachitas of the total salt formation", and "The scheme of isopachitas of the highest brand salt layer in the foot of central area of the field". It was calculated that the total volume of evaporated salt was around 38567 m^3 , of salt within the brine boundaries 36994 m^3, salt for domestic animals - 1339.8 m^3, high-grade salt -8699.5 m^3. The total brine volume was 28806 m^3 at the moment.

To find out the reserves of the brine and salt, the above-calculated brine and salt volumes were multiplied, respectively, by the brine and salt.

In November 3, 1996, the brine volume was 28.8 thousand m^3 or 34,6 thousand tons. These reserves could be referred to the category A+B in view of actual lingering consumption of as much as 30m^3 /day. The total salt stock is around 70.0 thousand tons for primary moisture content and 64.1thousand tons for air-dried condition. The reserves within the brine boundaries are equal to 70.0 and 61.5 thousand tons, respectively.

The total amount of high-grade salt was evaluated as a difference between preliminary calculated salt volume within the brine area and the sum of the rest salt. It was found to be 63.5 thousand tons at initial moisture content and 55.8 thousand tons for air-dried condition. In this stock, the amounts of for first and high-grade salt in the foot of the central part are equal to 16.4 and 14.5 thousand tons, respectively. Thus, the reserves of salt of first grade product are of 90% from the total stocks, which can be referred to the S.1 category.

Long-term practice of free brine evaporation method created a real basis for using lake-deflation hollows for utilisation of associated brines (and of natural concentrated salt brines). This technology is applicable for food and industrial quality salt production in the regions where the construction of underground reservoirs in salt deposit formations is carried out by washout method and the comprehensive environmental monitoring is organised.

Beside this problem, we analysed the possible use of water from Apsheron water-bearing horizon containing industrial concentration of iodine. This suggestion is actual both from environmental and economic points since production of sodium chloride requires usage of pure water the lack of which is notable for industrial consumption.

Mechanical mixing of potassium iodide and sodium chloride in accordance with GOST 4232 is applied in industry as a routine procedure for iodinated food salt production. Sodium thiosulfate is used as a stabiliser (GOST 27068). The weight fraction of sodium thiosulfate and iodine in iodinated food salt should be no more than $(25.5\pm5.0)\cdot10^{-3}$ and no less than 30-40 mg/kg, respectively.

The water-bearing Apsheron layer is spread throughout the Astrakban region at 105-119 m depth. In the region of Astrakhan gas condensate field, the Apsheron horizon exhibits as multilayer water pressurised system up to 200-m thick. The water-bearing horizons are formed by sand and pressurised water is localised at 10-20 in depth. The water contains sodium chloride with concentration of 22-35 g/l. The capacity of self-released wells is close to 34 m^3/hour whereas the temperature of effluent water ranges from 17.5 to 25.0 ^{0}C. The concentration of iodine and bromine in the water may vary in a wide range in horizontal and vertical direction approaching to industrial values. One of those regionally determined horizons at the depth of 250-300 in is used as a source for industrial water supply and of interest as a source of iodine-bromine containing water. The Apsheron water-bearing horizon is bedded by clay layer of Akchagvl sediments which plays the role of regional waterproof barrier of 90 -150-m width and prevents transfer of stratum waters from neighbouring horizons [8].

Chemical analysis of the water from exploratory well 313-B at Astrakhan gas condensate field performed for samples taken from Apsheron horizon showed its sodium-chloride composition with the mineralization equal to 32.0 mg/l: Cl^- - 98, $(Na^+ + K^+)$ - 69 mg-equiv. and pH = 6.9. Two bio-active components- bromine and iodine were found in concentrations of 55.0 and 18.0 mg/l, respectively, that makes it suitable for balneological therapy application. It was detected rather high content of ferric hydroxides in the water that yields flake-like sediment. No toxic elements such as lead, mercury, and chromium etc. as well as radioactive elements (at the level of background) were found [9].

Preliminary laboratory experiments were made on preparation of iodinated salt by salt deposit dissolving with water from Apsheron water-bearing horizon and subsequent evaporation of the brine at room temperature (concentration of the latter was 300.0 g/1). It was found that iodine content in the evaporated salt was 30.0 mg/kg whereas in the initial salt deposit this value was 1.7 mg/kg and in the brine - 12.0 mg/kg.

A sample of salt prepared by evaporation of the iodinated brine was examined at All-Russian Institute of Mineral Source (ARIMS) using x-ray analysis for detection of its mineral composition. The performed tests of the sample showed its heterophase nature that was the consequence of the admixing of gypsum, quartz, and magnesite to NaCl in concentration less than 1 w% from the host substance. The structural admixture of iodine was not detectable from diffraction patterns. The crystal lattice, actually, did not change after keeping a sample in ambient air, though the inclination of iodine into crystal lattice of sodium chloride should change the elementary cell at the iodine level about 0.05-0.1%. However, some kind of disordering was found in NaCl crystal structure in the initial sample before it was allowed to stay in. ambient air. It should be noted that after this procedure, the crystal structure of the NaCl sample is getting more perfect. This fact, together with the previous observation, proves that iodine, very probably, incorporates into crystal lattice of NaCl or its defects.

Evidently, the further study should be performed to know more about the space proximity of iodine in the crystal lattice of NaCl. Besides, it is of interest to determine the degree of iodine stability in the evaporated salt upon the influence of high and low temperatures, atmospheric falls winds, etc., during free evaporation of the brines.

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