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Preparation of Analytical Grade Sodium Chloride from Khewra Rock Salt

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Abstract: A three step process for the preparation of analytical grade sodium chloride from rock salt was developed. Three different samples of rock salts were collected from different sites of Khewra mines occurring in the eastern terminal part of the salt range of Punjab province of Pakistan. Samples were analyzed for impurities at ICP, which contain 93.6, 91.84 and 94.18% of NaCl respectively. Many impurities like Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, insoluble matter and chlorides of many metals in trace amounts were also present in the raw samples. A crude brine containing rock salt 310 g/L was prepared and filtered to remove insoluble impurities. Firstly, brine was recrystallized to decrease the concentration of soluble impurities. Recrystallized samples dried using centrifuge and oven contain 98.57, 98.28, 98.86% NaCl respectively. Secondly, primary treatment was employed using $BaCO_3$, NaOH and Na_2CO_3, which removed Ca^{2+}, Mg^{2+} and SO_4^{2-} up to ppm level. Concentrations of metals present in traces were removed up to ppb level during this step. Thirdly, ion exchange technique was used to remove Ca^{2+}, Mg^{2+} and SO_4^{2-} up to ppb level and SO_4^{2-} below 10 ppm. Final products contain 99.74, 99.45 and 99.74% NaCl respectively and traces of impurities also meet the analytical grade NaCl specification.

Key words: Khewra · Sodium chloride · Rock salt · Analytical grade · Chemical analysis

INTRODUCTION

Commercially available chemicals have different levels of purities. They may be of commercial grade having a higher level of impurities than reagent grade having negligible amount of impurities. Chemicals labeled "technical" or "commercial" are usually quite impure. An analytical reagent is a chemical almost free from impurities or having minimum level of impurities. Analytical grade sodium chloride is the pure form of sodium chloride having negligible amount of impurities. NaCl is most commonly used in food processing and biological products. This is also one of the most important raw materials of chemical industry [1].

Khewra Salt Mines is a salt mine located in Khewra in Jhelum District of Punjab, Pakistan, about 160 kilometers from Islamabad (capital) and 260 kilometers from Lahore. It is one of largest salt mine in the world. Situated in the foothills of the Salt Range, the Khewra Salt Mines are the oldest in the South Asia. Salt has been mined at Khewra since 320 BC, in an underground area of about 110 sq. km. Khewra salt mine has estimated total of 220 million tones of rock salt deposits. The production from the mine is about 325,000 tons salt per annum. Only 50% salt is extracted and 50% is left as pillers to keep the mountain. The salt-mine is 288 meters above sea level and extends around 730 meters inside the mountains from the mine-mouth. The cumulative length of all tunnels is more than 40 km. Salt occurs in a Pre-Cambrian deposit in the form of an irregular dome like structure. There are seven thick salt seams with a cumulative thickness of about 150 meters. Appearance of Khewra salt is transparent, white, pink and reddish to beef-color red [2-3].

Rock salt known as halite is the mineral form of common salt with the chemical composition sodium chloride (NaCl). It is available in deposits of rock salt, brines, saline lakes, marshes, sea water and saline earth. Rock salt is a common mineral, formed by the drying of enclosed bodies of salt water. Rock salt has certain applications, including-alkali manufacture, which uses the NaCl solution obtained directly from rock salt [4].

Sodium chloride is composed of two elements, sodium and chlorine. The percentage of these elements is Na 39.4%, Cl 60.6% in a unit formula. The rock salt is not always found in pure state. Calcium sulphate and magnesium sulphate are the major impurities present in industrial salt [5-6]. Impurities are mostly mechanical such as droplets of brine, gas bubbles and also inclusions of clay and organic matter, gypsum, KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgBr_2$, MgI_2 and $MgSO_4$. Salt is the most widely

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distributed mineral and has four distinct modes of occurrences: (1) Extensive deposits of rock salt; (2) salt solutions; (3) as sublimation products near volcanoes; and (4) as efflorescent, earthy crusts in arid regions. Out of these types only the first two are of commercial importance [7]. Synowiec [8] utilized the waste brine from an evaporative salt plant by means of spent solution from ammonia soda production. Rock salt is used for the production of purified salt by ordinary mining. Evaporated salt is the term applied to fine crystals of salt obtained by evaporating brines, either natural or manufactured. Solar salt is applied to salt deposits obtained from shallow; pounds by sailor and Aeolian evaporation [9].

The purpose of this work is to produce analytical grade sodium chloride from the available indigenous rock salt in Pakistan to meet the analytical grade specifications at low cost, in mass production and high purity as compared to others available in market. Further to our previous study on the production of table salt from indigenous rock salt[2] we have developed three steps process for the production of analytical grade sodium chloride in this paper.

EXPERIMENTAL

Materials used for the purification are sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), barium carbonate ($BaCO_3$), flocculant, weak acid cation exchange resin, strong basic anion exchange resin and HCl. All chemicals were of analytical grade and purchased from Merck (Germany).

Different samples of rock salt were collected from three different sites of Khewra mine and analyzed by conventional as well as instrumental method for the determination of different elements by using Inductively Coupled Plasma (ICP) spectrophotometer [10-11].

Preparation of Analytical Grade Sodium Chloride: Analytical grade NaCl produced by three steps displayed in Figure 1.

Brine Preparation and Recrystallization: In 1 liter distilled water 310g of rock salt was added and heated it up to 65°C along with stirring with the help of a magnetic stirrer for complete dissolution. After complete dissolution, brine was filtered with Wattmann filer paper to remove mud and other insoluble matter.

Recrystallization was carried by concentrating the brine by evaporation. The brine was concentrated to such a point that maximum of the salt crystals were separated out. Evaporation proceeds until the brine density reaches 1.25 or 1.26 g/ml. This corresponds to precipitation of 74-80% of the NaCl. In the next step, the crystals were separated from mother-liquor with the help of centrifuges and subjected drying. This step decreased the concentration of water soluble impurities in brine. Recrystallization removed nearly 80-90% of magnesium and 55-65% of calcium. The recrystallized samples were analyzed for impurities like SO_4^{2-} as sulphur, Ca^{2+}, Mg^{2+}, K^+ and other metallic impurities at ICP.

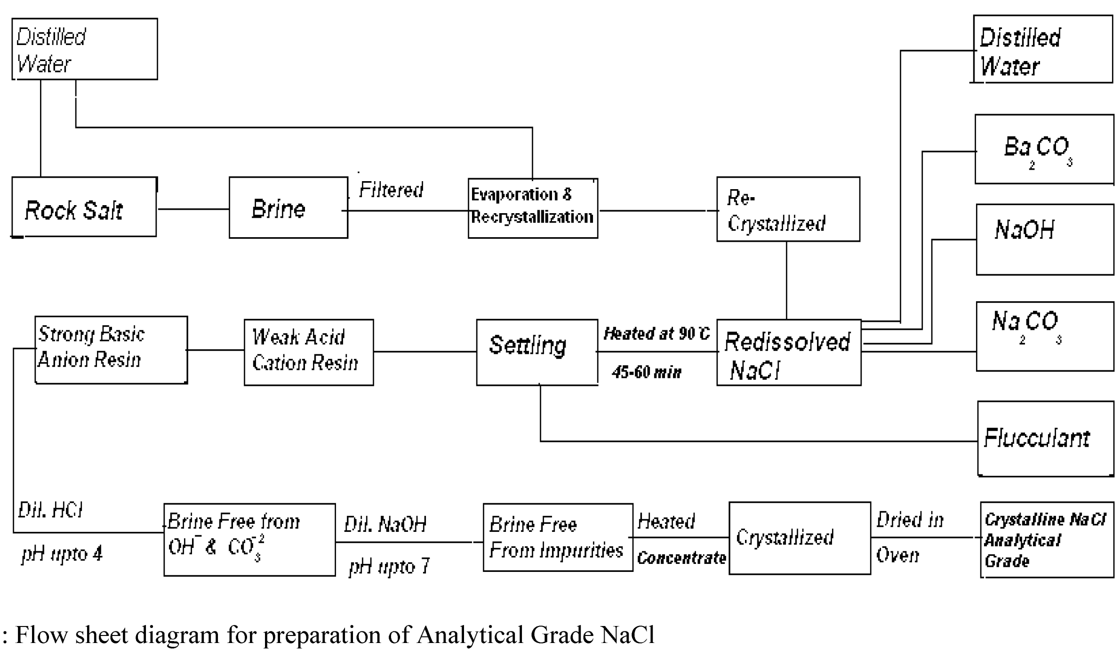

Fig. 1: Flow sheet diagram for preparation of Analytical Grade NaCl

Primary Treatment: The recrystallized NaCl prepared in step 1 was again dissolved in the distilled and de-ionized water and added calculated amount of barium carbonate in equal molar ratio slight excess than the amount of sulphates present. Barium carbonate reacts with sodium sulphate to form $Na_2 CO_3$ and $BaSO_4$. $BaSO_4$ is water insoluble and hence precipitated out. The mixture was heated after the addition of barium carbonate for 15 minutes at 80°C.

Addition of NaOH convert the $MgCl_2$ and $MgBr_2$ into insoluble $Mg(OH)_2$ which is precipitated out. Sodium carbonate was added to remove calcium. Addition of sodium carbonate converts soluble $CaCl_2$ into insoluble $CaCO_3$ which is precipitated out. Heating was continued along with stirring with the help of a magnetic stirrer for almost 45 minutes. A turbid, milky white solution was obtained containing insoluble $CaCO_3$, $Mg (OH)_2$, $BaSO_4$ and other hydroxides of several trace metals.

Polyacrylamide was added as a flocculent or coagulating agent, which started dissolving slowly. When a clear solution was obtained, 20ml of this solution was added to the beaker containing milky white solution of brine. Polyacrylamide coagulated quickly and precipitated and settled down at the bottom. No stirring was done after the addition of flocculant. Impurities were settled at the bottom and clear brine was obtained and was then filtered twice with the help of a Whatmann filter paper of pore size 0.4μm. Maximum concentration of of trace metals were removed at this stage. Only Ca^{2+}, Mg^{2+}, K^+ and $SO_4{}^{2-}$ were present at ppm level.

Secondary Treatment: Ion exchange resins were used for secondary treatment to remove the impurities like Ca^{2+}, Mg^{2+}, K^+ and $SO_4{}^{2-}$ which could not be significantly removed by primary treatment as shown by the analytical results.

Primary treated brine was passed through column of weak acid cation exchange resin for the removal of Ca^{2+}, Mg^{2+} and K^+. For this, pH of the brine was maintained in between 9.0-10.0 for effective removal of impurities. First, weak acid cation exchange resin was regenerated by passing 4% NaOH solution. A column of diameter 1 inches and volume 50ml weak acid cation exchange resin was prepared and 2 liters of 4% NaOH solution was passed through it at such a speed that it took 1 hour. After regeneration, brine of pH 9.0-10.0 was passed through the column very slowly. The resin was regenerated again after passing each sample.

RESULTS AND DISCUSSION

Chemical composition of rock salt before the treatment process (Table 1, 2) and refined salt after the treatment processes of recrystallization, primary treatment, secondary treatment was determined and presented in Table 3, 4 and 5 respectively. Chemical analysis shows that raw material contains NaCl (91.84- 94.18%), Ca (0.84-1.12%), Mg (0.438-0.94%), K (0.7334-1.3%) and sulphate (1.63-2.016) (Table 1).

After recrystallization, three samples contain 98.57, 98.28, 98.865% NaCl, respectively Recrystallization removes nearly 80-90% of magnesium and 55-65% of calcium. K^+ and other trace metals are also removed in this step in reasonable amount (Table 3). The main advantage of this step is that it removes impurities without any chemical used and so it is much cost effective.

Primary treatment removed all the trace metals upto ppb level and having 99.16, 99.16, 99.45% NaCl, respectively. This also removed calcium, magnesium and sulphates to a reasonable extent. Almost maximum of

Table 1: Chemical analysis of three rock salt samples (wt% on dry bases)

Components	Sample-1	Sample -2	Sample -3
NaCl	93.6	91.84	94.18
Ca^{2+}	0.8492	1.12	0.934
Mg^{2+}	0.4384	0.8479	0.9744
K^+	1.3	1.67	0.7334
$SO_4{}^{2-}$	2.016	1.632	2.16

Table 2: Chemical analysis of trace metals present in rock salt samples (mg/kg dry bases)

Symbol of element	Sample -1	Sample -2	Sample -3
Ag (Silver)	0.6317	0.5943	0.2146
Al (Aluminium)	26.121	38.127	28.51
B (Boron)	19.5	29.193	41.484
Ba (Barium)	25.157	13.276	23.987
Bi (Bismuth)	7.141	13.436	8.6493
Cd (Cadmium)	8.947	0.6343	5.8645
Co (Cobalt)	0.7659	1.049	7.9849
Cr (Chromium)	3.7692	1.2234	1.379
Cu (Copper)	1.9841	2.3167	19.48
Fe (Iron)	49.844	24.89	19.65
Ga (Gallium)	9.7819	4.6645	7.762
In (Indium)	6.7095	5.9634	4.958
Li (Lithium)	3.8214	5.9418	7.8943
Mn (Manganese)	6.7482	9.0567	3.8054
Ni (Nickel)	6.0962	4.7856	0.9834
Pb (Lead)	9.7143	17.743	28.976
Sr (Strontium)	37.894	61.567	34.567
Tl (Tellurium)	11.56	18.765	41.987
Zn (Zinc)	17.548	6.8954	17.896

Table 3: Amount of trace metals present in recrystallized samples (mg/kg on dry bases)

Components	Sample-1	Sample-2	Sampele-3
NaCl	98.57%	98.28%	98.86%
Ca^{2+}	0.3576	0.4979	0.0919
Mg^{2+}	0.1649	0.1474	0.1346
K^{+}	0.7687	0.2584	0.2934
SO_4^{2-}	0.4194	0.3513	0.4692
Ag (Silver)	0.1815	0.3682	0.0573
Al (Aluminium)	11.687	21.455	21.985
B (Boron)	1.6684	17.531	21.671
Ba (Barium)	19.315	9.7831	11.855
Bi (Bismuth)	4.1543	8.6785	3.7459
Cd (Cadmium)	0.4527	0.2877	3.8976
Co (Cobalt)	0.1186	2.2849	5.8454
Cr (Chromium)	0.6229	0.4674	0.7453
Cu (Copper)	1.1385	0.2698	17.829
Fe (Iron)	33.957	17.938	14.177
Ga (Galium)	6.2864	1.4587	4.8825
In (Indium)	5.9654	4.9341	3.4561
Li (Lithium)	2.7632	1.9056	1.4152
Mn (Manganese)	5.8152	2.4573	2.6049
Ni (Nickle)	5.8462	2.2934	0.2783
Pb (Lead)	0.0459	0.1215	3.8851
Sr (Strontium)	29.234	35.118	8.8762
Tl (Tellurium)	9.1583	12.891	9.2849
Zn (Zinc)	16.529	2.6896	12.519

Table 4: Chemical analysis of purified salt samples after primary treatment (mg/kg on dry bases)

Components	Sample-1	Sample-2	Sample-3
NaCl	99.16%	99.16%	99.45%
Ca^{2+}	7.1749	4.5954	3.8762
Mg^{2+}	4.6239	0.0071	0.4418
K^{+}	786	1228	2462
SO_4^{2-}	298.39	116.22	204.87
Ag (Silver)	0.0519	0.0005	0.0031
Al (Aluminium)	0.0093	0.0058	0.0058
B (Boron)	0.0151	0.0075	0.0634
Ba (Barium)	0.0813	0.0091	0.0659
Bi (Bismuth)	0.0067	0.0018	0.0078
Cd (Cadmium)	0.0052	0.0043	0.0008
Co (Cobalt)	0.0091	0.0069	0.0457
Cr (Chromium)	0.0041 m	0.0092	0.0084
Cu (Copper)	0.0046	0.0019	0.0293
Fe (Iron)	0.0015	0.0317	0.0742
Ga (Galium)	0.0074	0.0094	0.0829
In (Indium)	0.0019	0.0073	0.0562
Li (Lithium)	0.0082	0.0791	0.0152
Mn (Manganese)	0.0074	2.5628	0.0043
Ni (Nickle)	0.0183	0.0003	0.0984
Pb (Lead)	0.0007	0.0072	0.0085
Sr (Strontium)	0.0069	0.0023	0.0061
Tl (Tellurium)	0.0053	0.0119	0.0047
Zn (Zinc)	0.0091	0.0008	0.0194

Table 5: Chemical analysis of purified salt samples after secondary treatment (mg/kg on dry bases)

Component	Sample -1	Sample -2	Sample -3
NaCl	99.74%	99.45%	99.74%
Ca^{2+}	0.0159	0.0043	0.0393
Mg^{2+}	0.0394	0.0008	0.0062
K^{+}	0.0684	0.0861	0.0571
SO_4^{2-}	5.5173	2.7561	2.1906
Ag (Silver)	0.0411	0.0003	0.0027
Al (Aluminium)	0.0071	0.0045	0.0047
B (Boron)	0.0146	0.0059	0.0567
Ba (Barium)	0.0714	0.0086	0.0653
Bi (Bismuth)	0.0081	0.0012	0.0024
Cd (Cadmium)	0.005	0.0047	0.0005
Co (Cobalt)	0.0071	0.0057	0.0412
Cr (Chromium)	0.0036	0.0089	0.0059
Cu (Copper)	0.0042	0.0011	0.0221
Fe (Iron)	0.0011	0.0324	0.0749
Ga (Gallium)	0.0066	0.0045	0.0827
In (Indium)	0.0011	0.0064	0.0504
Li (Lithium)	0.0077	0.0499	0.0141
Mn (Manganese)	0.0061	0.0079	0.0021
Ni (Nickel)	0.0138	0.0002	0.0891
Pb (Lead)	0.0005	0.002	0.0046
Sr (Strontium)	0.0051	0.0014	0.0051
Tl (Tellurium)	0.004	0.0181	0.0036
Zn (Zinc)	0.0081	0.0006	0.0129

the trace metals are removed in this step and there is no need for further treatment to remove trace metals. But the impurities of Ca^{2+}, Mg^{2+}, K^{+} and SO_4^{2-} are still present that do not meet the analytical reagents specification (Table 4). A further treatment is given to remove these impurities upto a level that meet the specification.

After secondary treatment process, the required composition of pure salt has been achieved to the standard level of purity. This composition contains NaCl (99.74%), Ca (0.004-0.03%), Mg (0.006-0.039%), K (0.05-0.06%) and sulphate (2.19-5.51%) with other trace metals Fe, Zn and Pb etc (Table 5).

Comparison of purified salt with analytical grade NaCl of some well known companies A and B is shown in Table 6. This shows that analytical grade NaCl of A contains NaCl (>99.5%), while B contains (>99.0%) whereas our purified salt contains (99.74%). Other impurities like SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^{+}, Fe and Pb^{2+} are also present in minimum amounts as compared to A and B. The results show that our method is more appropriate for the production of analytical grade sodium chloride from rock salt.

Table 6: Comparison of secondary treated samples with Analytical Grade NaCl with available in the market (A and B)

Components	Sample-1	Sample -2	Sample -3	A	B
NaCl	99.74%	99.45%	99.74%	>99.0%	>99.5%
SO_4^{2-}	0.00%	0.00%	0.00%	≤0.004%	≤0.001%
Ba^{2+}	0.00%	0.00%	0.000006	Passes Test	≤0.0002%
Ca^{2+}	0.00%	0.00%	0.00%	≤0.002%	0.00%
Mg^{2+}	0.00%	0.00%	0.00%	≤0.001%	0.00%
K^{+}	0.00%	0.00%	0.00%	≤0.005%	0.00%
Fe (Iron)	0.0011ppm	0.0324ppm	0.0749ppm	≤2 ppm	≤0.05ppm
Pb^{2+}	0.0005ppm	0.002ppm	0.0046ppm	≤5 ppm	≤0.005ppm

NaCl, with out impurities, is an essential element of diet and used in cooking. It is also used in many brands of shampoos and has been used as cleansing agent for cleaning household surfaces by rubbing with sodium chloride. Many living organisms cannot live in the salty environment because the water from their cells is drawn out by osmosis. Due to this reason salt can be used as a preservative for foods and other biological products.

Sodium Chloride has a wide range of synthetic uses. It is the valuable raw material for the synthesis of many industrial chemicals. It is a raw material used for the manufacturing of caustic soda, chlorine gas, soda ash, sodium peroxide and many other chemicals. Sodium carbonate is another important product of commercial use. It is manufactured commercially from sodium chloride by Solvay process. Sodium chloride is also used in the manufacturing of metallic sodium, sodium peroxide (bleaching agent used in textile industries), sodium sulfate and many more products. Utilization of NaCl can be increased after getting its purity and large scale production form indigenous raw material and this can be achieved by using our process of manufacturing of NaCl.

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