

An Improved Method for the Preparation of Analytical Grade Sodium Chloride from Khewra Rock Salt

¹Attique ur Rahman, ¹Amjad Islam and ¹Muhammad Akhyar Farrukh

¹Department of Chemistry, GC. University, Katchery Road, Lahore-54000, Pakistan

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 locating in the eastern terminal part of the salt range of Punjab province of Pakistan. Impurities in the sample were analyzed with Inductively Coupled Plasma (ICP), which contain 93.600, 91.840 and 94.180% 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 98.570, 98.280, 98.860% 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 99.740, 99.450 and 99.740% 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. 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 pillars 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 [2-4].

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 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

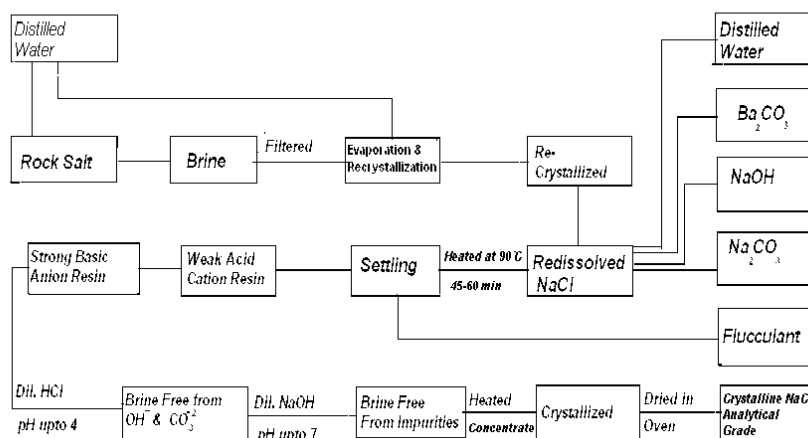


Fig. 1: Flow sheet diagram for preparation of Analytical Grade NaCl

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 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, purchased from Merck (Germany) and used without further purification.

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, 310 g of rock salt was added and heated up to 65°C along with stirring for complete dissolution. After complete dissolution, brine was filtered

with Wattmann filter paper to remove mud and other insoluble matter.

The brine was concentrated to such a point that maximum of the salt crystals were separated out. Evaporation proceeds until the brine density reaches 1.25-1.26 g/mL which corresponds to precipitation of 74-80% of NaCl. In the next step, the crystals were separated from mother-liquor with the help of centrifuges and subjected drying. 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 with ICP.

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_2CO_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 $\text{Mg}(\text{OH})_2$ which is precipitated out. 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 , $\text{Mg}(\text{OH})_2$, 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, 20 mL of this

solution was added to the beaker containing milky white solution of brine. 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 trace metals were removed at this stage. Only Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻ were present at ppm level.

Secondary Treatment: Ion exchange resins were used for secondary treatment to remove the impurities like Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻ 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 Ca²⁺, Mg²⁺ 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 50 mL 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. 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 (91.840- 94.180%), Ca (0.849-1.120%), Mg(0.438-0.974%),K (0.733-1.300%)and sulphate (1.632-2.160) (Table 1).

After recrystallization, three samples contain 98.570, 98.280, 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 99.160, 99.160, 99.450% NaCl, respectively. This also removed calcium, magnesium and sulphates to a reasonable extent. Almost maximum of the trace metals are removed in this step and there is no need for further treatment to remove trace metals. But the impurities of Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻ are still present that

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

Components	Sample-1	Sample -2	Sample -3
NaCl	93.600	91.840	94.180
Ca ²⁺	0.849	1.120	0.934
Mg ²⁺	0.438	0.848	0.974
K ⁺	1.300	1.670	0.733
SO ₄ ²⁻	2.016	1.632	2.160

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

Symbol of element	Sample -1	Sample -2	Sample -3
Ag (Silver)	0.632	0.594	0.215
Al (Aluminium)	26.121	38.127	28.510
B (Boron)	19.500	29.193	41.484
Ba (Barium)	25.157	13.276	23.987
Bi (Bismuth)	7.141	13.436	8.649
Cd (Cadmium)	8.947	0.634	5.865
Co (Cobalt)	0.766	1.049	7.985
Cr (Chromium)	3.769	1.223	1.379
Cu (Copper)	1.984	2.317	19.480
Fe (Iron)	49.844	24.890	19.650
Ga (Gallium)	9.782	4.665	7.762
In (Indium)	6.710	5.963	4.958
Li (Lithium)	3.821	5.942	7.894
Mn (Manganese)	6.748	9.056	3.805
Ni (Nickel)	6.096	4.786	0.983
Pb (Lead)	9.714	17.743	28.976
Sr (Strontium)	37.894	61.567	34.567
Tl (Tellurium)	11.560	18.765	41.987
Zn (Zinc)	17.548	6.895	17.896

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

Components	Sample-1	Sample-2	Sample-3
NaCl	98.570%	98.280%	98.860%
Ca ²⁺	0.358	0.498	0.092
Mg ²⁺	0.165	0.147	0.135
K ⁺	0.769	0.258	0.293
SO ₄ ²⁻	0.419	0.351	0.469
Ag (Silver)	0.182	0.368	0.057
Al (Aluminium)	11.687	21.455	21.985
B (Boron)	1.668	17.531	21.671
Ba (Barium)	19.315	9.783	11.855
Bi (Bismuth)	4.154	8.679	3.746
Cd (Cadmium)	0.453	0.288	3.898
Co (Cobalt)	0.119	2.285	5.845
Cr (Chromium)	0.623	0.467	0.745
Cu (Copper)	1.139	0.270	17.829
Fe (Iron)	33.957	17.938	14.177
Ga (Gallium)	6.286	1.459	4.883
In (Indium)	5.965	4.934	3.456
Li (Lithium)	2.763	1.906	1.415
Mn (Manganese)	5.815	2.457	2.605
Ni (Nickel)	5.846	2.293	0.278
Pb (Lead)	0.046	0.122	3.885
Sr (Strontium)	29.234	35.118	8.876
Tl (Tellurium)	9.158	12.891	9.285
Zn (Zinc)	16.529	2.690	12.519

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

Components	Sample-1	Sample-2	Sample-3
NaCl	99.160%	99.160%	99.450%
Ca ²⁺	7.175	4.595	3.8762
Mg ²⁺	4.624	0.007	0.442
K ⁺	786.001	1228.002	2462.001
SO ₄ ²⁻	298.390	116.220	204.870
Ag (Silver)	0.052	0.001	0.003
Al (Aluminium)	0.010	0.006	0.006
B (Boron)	0.015	0.008	0.063
Ba (Barium)	0.081	0.009	0.066
Bi (Bismuth)	0.007	0.002	0.008
Cd (Cadmium)	0.005	0.004	0.001
Co (Cobalt)	0.009	0.007	0.046
Cr (Chromium)	0.004	0.009	0.008
Cu (Copper)	0.005	0.002	0.029
Fe (Iron)	0.002	0.032	0.074
Ga (Gallium)	0.007	0.009	0.083
In (Indium)	0.002	0.007	0.056
Li (Lithium)	0.008	0.079	0.015
Mn (Manganese)	0.007	2.563	0.004
Ni (Nickle)	0.018	0.0003	0.098
Pb (Lead)	0.0007	0.007	0.009
Sr (Strontium)	0.007	0.002	0.006
Tl (Tellurium)	0.005	0.012	0.005
Zn (Zinc)	0.009	0.001	0.019

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

Components	Sample -1	Sample -2	Sample -3
NaCl	99.740%	99.450%	99.740%
Ca ²⁺	0.016	0.004	0.039
Mg ²⁺	0.039	0.001	0.006
K ⁺	0.068	0.086	0.057
SO ₄ ²⁻	5.517	2.756	2.191
Ag (Silver)	0.041	0.0003	0.003
Al (Aluminium)	0.007	0.005	0.005
B (Boron)	0.015	0.006	0.057
Ba (Barium)	0.071	0.009	0.065
Bi (Bismuth)	0.008	0.001	0.002
Cd (Cadmium)	0.005	0.005	0.001
Co (Cobalt)	0.007	0.006	0.041
Cr (Chromium)	0.004	0.009	0.006
Cu (Copper)	0.004	0.001	0.022
Fe (Iron)	0.001	0.032	0.075
Ga (Gallium)	0.007	0.005	0.083
In (Indium)	0.001	0.006	0.050
Li (Lithium)	0.008	0.05	0.014
Mn (Manganese)	0.006	0.008	0.002
Ni (Nickel)	0.014	0.0002	0.089
Pb (Lead)	0.0005	0.002	0.005
Sr (Strontium)	0.005	0.001	0.005
Tl (Tellurium)	0.004	0.018	0.004
Zn (Zinc)	0.008	0.001	0.013

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	99.740%	99.450%	99.740%	>99.000 %	>99.500 %
SO ₄ ²⁻	5.5×10 ⁴ %	2.0×10 ⁴ %	2.0×10 ⁴ %	≤4.0×10 ³ %	≤1.0×10 ³ %
Ba ²⁺	7.0×10 ⁶ %	8.0×10 ⁷ %	6.0×10 ⁶ %	Passes Test	≤2.0×10 ⁴ %
Ca ²⁺	1.0×10 ⁶ %	4.0×10 ⁸ %	3.0×10 ⁶ %	≤2.0×10 ³ %	1.0×10 ² %
Mg ²⁺	3.0×10 ⁶ %	7.0×10 ⁷ %	6.0×10 ⁷ %	≤1.0×10 ³ %	5.0×10 ² %
K ⁺	6.0×10 ⁶ %	8.0×10 ⁶ %	5.0×10 ⁶ %	≤5.0×10 ³ %	5.0×10 ⁴ %
Fe (Iron)	0.0011 ppm	0.0324 ppm	0.0749 ppm	≤2 ppm	≤0.05 ppm
Pb ²⁺	0.0005 ppm	0.002 ppm	0.0046 ppm	≤5 ppm	≤0.005 ppm

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 (99.740%), Ca (0.004-0.039%), Mg (0.006-0.039%), K (0.057-0.086%) and sulphate (2.191-5.517%) 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 (99.740%). Other

impurities like SO₄²⁻, Ca²⁺, Mg²⁺, K⁺, Fe and Pb²⁺ 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.

NaCl, without 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 from indigenous raw material and this can be achieved by using our process of manufacturing of NaCl.

ACKNOWLEDGEMENTS

The authors would like to acknowledge GC University Lahore for support and financial assistance through research grant.

REFERENCES

1. Kilic, O. and M.A. Kilic, 2005. Recovery of salt co-products during the salt production from brine. *Desalination*, 186: 11-19.
2. Qadir, H., M.A. Farrukh and M. Aurangzaib, 2005. Production of Table Salt from Kohat Rock Salt. *J. Appl. Sci.*, 5: 12-14.
3. Quddus, A.S., 1992. Punjab, the land of beauty, love and mysticism, Royal Book Co., the University of Michigan, pp: 405.
4. Brien'O, F. Thomas, 2005. Handbook of Chlor-Alkali Technology, Vol. 1, Springer Science+Business Media, Inc.
5. Desai, S.A., D.V. Choughule, S.S. Patil and M. Sriram, 1999. Chromatographic determination of anions in industrial salt and sodium chloride brines used in chlor-alkali industry. *J. Chromatogr. A.*, 841: 55-62.
6. Madaeni, S.S and V. Kazemi, 2008. Treatment of saturated brine in chlor-alkali process using membranes. *Sep. Purif. Technol.*, 61: 68-74.
7. Ladoo, Raymond B. and M.W. Myers, 1951. Non Metallic Minerals. McGraw Hill book Company Inc. 2nd eds., pp: 436-437.
8. Synowiec, M.P. and B. Bunikowska, 2005. Application of crystallization with chemical reaction in the process of waste brine purifying in evaporative sodium chloride production. *Ind. Eng. Chem. Res.*, 44: 2273-2280.
9. Geo, E.R., 1944. The age of saline series of Punjab and Kohat. In symposium on the age of saline series in the salt range of Punjab. *Proc. Nat. Acad. Sci. India*, 14: 269-312.
10. Scott, W.W. and N.H. Furman, 1962. Standard Methods of Chemical Analysis, Vol. 1, 6th Edn., D. Van. Nostrand Company Inc, Princeton, New Jersey, New York.
11. Jeffry, G.H., J. Bassett, J. Mendhan and R.C. Denney, 1994. Vogel's, Textbook of Quantitative Chemical Analysis, 5th Edn., Longman Group London.