Chemical Evaluation of Major Salt Deposits of Pakistan

QAZI MUHAMMAD SHARIF*, MUMTAZ HUSSAIN AND MUHAMMAD TAHIR HUSSAIN
P.C.S.I.R Laboratories Complex Peshawar-25120, Pakistan

(Received 20th July 2006, revised 18th December 2006)

Summary: Seven salt samples from major salt deposits were analyzed for sodium chloride, moisture content, water insoluble matter, calcium, magnesium, sulphate, potassium and trace elements respectively. Except Kohat rock salt and Khaller salt where insoluble matter and other impurities were high, other salt samples contained permissible limits of insoluble matter and other impurities as per Codex Alimentarius Specifications. Trace elements like zinc, iron, copper, manganese, chromium and lead were analyzed by atomic absorption spectrophotometer. Metal load in salt samples of all sources are within limits as per RDA specifications for respective metals. The geological settings including nature, origin of the salt deposits and impacts of impurities present in salt samples on human health and other chemical industries have also been discussed in this study.

Introduction

Pakistan is known for its famous salt ranges stretching from Kalabagh to Jehlum covering the districts of Mianwali, Chakwal and Jehlum in the province of Punjab. In the province of N.W.F.P, Geological survey has determined the existence of 10.54 billion tons of rock salt reserves at Bahadur Khel in district Kohat [1]. The total reserves of rock salt deposits in Pakistan are inexhaustible [2-6].

Pakistan is one of the very few countries that have been bestowed with all types of available salt in the world i.e. Rock salt, Sea salt and Salt lake. Salt mines occurring in the salt range formation are one of the oldest mines of the subcontinent. Right from the eastern terminal part of the Salt Range [7], the plugging of the salt has cropped out at several places like Khewra, Warcha, Kalabagh, Jatta and Bahadur Khel from which several thousand tons of salt is being mined annually [8]. Large deposits of salt occur at a number of places in N.W.F.P. Important salt mines are those of Jatta, Bahadur Khel and Karak. All these deposits are accessible by roads from Bannu-Kohat metalled road [9].

On the basis of quality of rock salt, four different types of crystals are found here, including pink, white, soft lumps and soft crystalline lump. The overall scenario at the salt range mining site is very under utilized and production is too small keeping in view the deposits of this most important mineral. The total production estimation of all mines is estimated around 600,000 tons annually. Salt lake is excellent in quality and quantity. The lakes are located some 250 Km in the north-east of Karachi city. An amount of 500 tons is extracted from these 10 to 12 lakes on daily basis making the yearly average production to around 150,000 tons.

Geological Settings

Nature and Origin of the Salt Deposits of Pakistan

The Kohat salt is also considered to be a normal bedded deposit occurring below Kuldana formation (Eocene) in the cores of various tightly folded "anticline" bounded on each side by very steep to vertical Eocene and Sizalik (Miocene to Pleistocene) strata. In the Geological Survey of Pakistan stratigraphy, the Kohat rock salt near Bahadur Khel out crops over a length of about 12 Km and width of about half a Km. Early Eocene age has been assigned to Bahadur Khel salt.

The Salt Range is pink red in general while that of Kohat salt is white grey. The Salt Range salt is generally coarse crystalline to massive rather compact while Kohat salt is generally fine to medium crystalline, friable and loose rather sugary. A special feature of Kohat salt is its porphyritic texture, which is unusual in Salt Range. Situated at the foothills of the Salt Range, Khewra Salt Mines are the oldest in the salt mining history of the sub-continent. Salt occurs in the form of an irregular dome like structure. There are seven thick salt seams with cumulative thickness of about 150 meters. Salt is transparent, white, pink, and reddish to beef-colored. In certain horizons it is crystalline.

*To whom all correspondence should be addressed.

Inside the mine there are beautiful alternate bands of red and white salt. There are 18 working levels. Cumulative length of all drivages is more than 40 km.

Sodium Chloride regulates the acid/ alkali balance in the body. It is also necessary for the production of gastric acid, which is a component of hydrochloric acid. It has important physiological functions. It is an important constituent of blood and also serves to regulate the potassium content of the body. The human body contains 2.5 gram of salt per kg weight. It needs to be continuously replaced since the kidneys regularly excrete salt as 2% solution, from which it follows that man cannot drink seawater because its salt content (3.5 %) is higher than this [10].

Salt is used in the diet of humans and animals as well as for preventing heat cramps and other medicinal purposes. One common medicinal use is for isotonic salt solutions. It is commonly used in preserving and seasoning foods such as in curing meat, other meat products, curing fish, making pickles, preserving other vegetables, canning vegetables and meat baking and many other familiar household uses [11].

Industrially salt is used for the manufacturing of calcium chloride, chlorine dioxide, chlorine gas, sodium chlorate, sodiumflourosilicate, sodium hypochlorate, sodium perchlorate, soda ash, sodium metal, sodium sulfate, hydrochloric acid and caustic soda etc. It is also used as antifreeze in ice cream making and refrigerating brines etc [12].

Many other chemical analysis and evaluation of salt deposits of Pakistan have been reported [1, 2, 4-9] but impacts of impurities present in salt samples on human health and other chemical industries have not been yet described anywhere. Seven salt samples were analyzed from different localities of Pakistan including Kohat, Khewra, Khallar and Lake salt in order to present the chemical composition of these salt deposits. Different salt quality parameters and their effects on human health and other industries are also discussed in the present study.

Results and Discussion

The salt samples were collected from different sites and were analyzed by conventional as well as by instrumental methods [13-17].

The parameters which were analyzed for salt samples are moisture content, water insoluble matter, calcium (Ca^{+2}), magnesium (Mg^{+2}), sulphate $(SO_4)^{-2}$, chloride (Cl^-), sodium (Na^+) and potassium (K^+). The results are given in Table-1. This table shows that the moisture content range from 0.09 % (Red salt Khewra) to 0.31 % (Lake salt Tharparker), water insoluble 0.30 % (Lake Salt Tharparker) to 5.00 % (Khallar Salt, Kallar Kahar), Calcium 0.20 % (White Hard Salt Khewra) to 1.75 % (Rock Salt Kohat), Magnesium 0.09 % (White Crystal Salt Khewra) to 1.26 % (Kallar salt), Sulphate 0.25 % (White Hard Salt Khewra) to 8.35 % (Khallar Salt) and Potassium 0.002 % (Rock salt Kohat) to 0.80 % (White Hard salt Khewra) respectively. All values are within limits as per Codex Alimentarius [18]. The graphical presentation of salt quality parameters is as shown in Fig. 1 and 2.

On the other hand trace elements (Fe, Zn, Cu, Mn, Cr, Pb, and Cd) in the given salt samples were analyzed with help of atomic absorption spectrophotometer. The results are given in Table-2. Heavy metals have great significance due to their tendency to accommodate in human organs over a prolong period of time. The presence of heavy metals beyond the allowed upper and lower limits can cause

Table-1: Different analytical parameters of the given salt samples.

S. No.	Name and source	Sodium chloride as NaCl %*	Moisture %	Water Insoluble %	Calcium as Ca^{++} %	Magnesium as Mg^{++} %	Sulfate as SO_4 %	Potassium as K^+ %
1.	Rock salt (Kohat)	92.02	0.12	3.50	1.75	0.16	2.15	0.002
2.	Pinkish salt (Khewra)	98.30	0.11	0.40	0.30	0.12	0.28	0.046
3.	Red salt (Khewra)	98.10	0.09	0.50	0.25	0.12	0.58	0.045
4.	White hard salt(Khewra)	97.55	0.12	0.80	0.20	0.12	0.25	0.800
5.	White crystal salt (Khewra)	98.15	0.13	0.90	0.20	0.09	0.33	0.204
6.	Khallar salt (KallarKahar)	84.15	0.22	5.00	0.90	1.26	8.35	0.024
7.	Lake salt (Tharparker)	98.25	0.31	0.30	0.30	0.12	0.50	0.006

* Purity determined as per ASTM standards E 534-98 (2002).

Table-2: Trace element analysis of the given salt samples (mg/ Kg).

S. No.	Name and source	Fe	Zn	Cu	Mn	Cr	Pb	Cd
1.	Rock salt (Kohat)	0.62	0.18	0.01	0.00	0.34	0.03	0.00
2.	Pinkish salt (Khewra)	0.24	0.12	0.00	0.00	0.36	0.10	0.00
3.	Red salt (Khewra)	0.46	0.13	0.01	0.00	0.37	0.02	0.00
4.	White hard salt (Khewra)	0.97	0.19	0.01	0.06	0.19	0.02	0.00
5.	White crystal salt (Khewra)	0.48	0.20	0.03	0.00	0.37	0.03	0.00
6.	Khallar salt (KallarKahar)	0.29	0.07	0.01	0.00	0.33	0.03	0.00
7.	Lake salt (Tharparker)	1.16	0.11	0.02	0.00	0.40	0.03	0.00

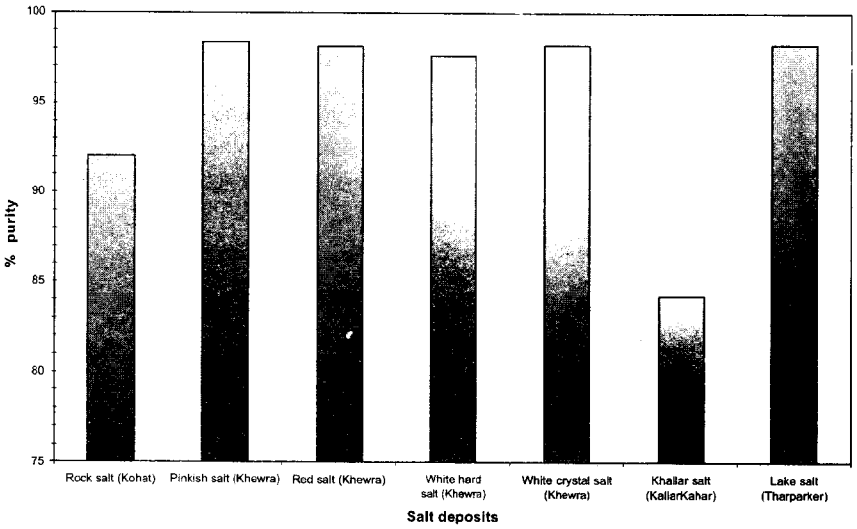

Fig. 1: Graph of % purity of major salt deposits.

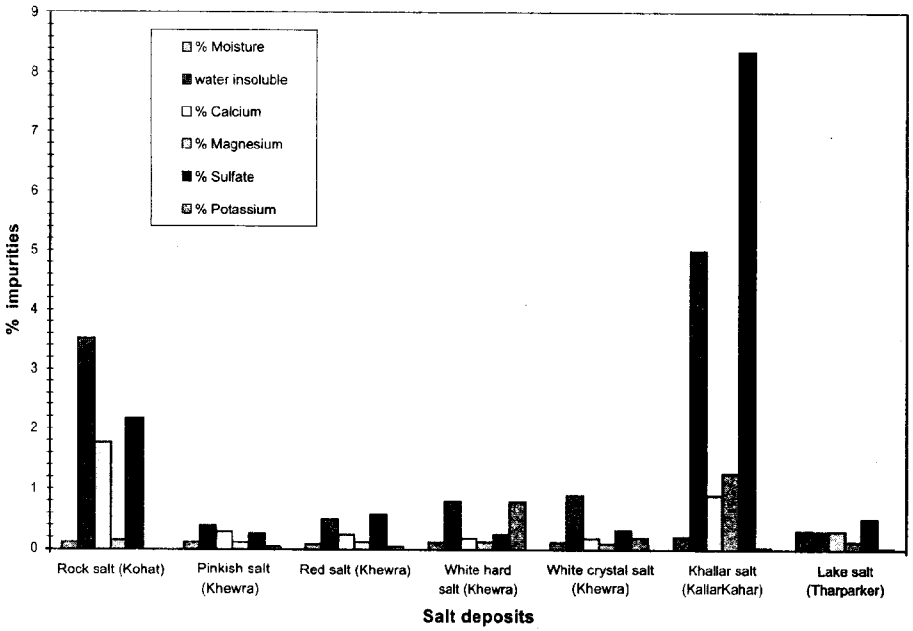

Fig. 2: Graph of impurities Vs salt deposits.

metabolic disturbance. Thus both the deficiency and excess of heavy metals may produce undesirable effects [19].

Iron (Fe)

Iron plays an important role in human body metabolism. It acts as a catalyst and is present in amount greater than that of any other trace element. The heme pigments, hemoglobins in erythrocytes and myoglobins in muscle function as oxygen carrier [20]. Recommended dietary allowances (RDA) for iron is 50-400 μg/ day. Thus results of all samples are in accordance with RDA value.

Copper (Cu)

Copper is an essential trace element for normal biological activities of aminoxide and tyrosinase enzymes. Excessive intake of copper may cause heamolysis, hepatotoxic and nephrotoxic effects [21]. Recommended dietary allowances (RDA) for Copper is 150-600 μg / day. Thus results of all samples are less than RDA value for Copper.

Manganese (Mn)

Manganese is another essential element. Its uptake is controlled metabolically [22]. It is essential for normal growth, skeletal formation and for normal reproductive function in mammals and poultary. Its deficiency causes diabetes, nervous instability, disorder of bony cartilaginous growth in infant and rheumatic arthritis in adults [23]. Recommended dietary allowances (RDA) for Manganese is 20-90 μ g/ day. Manganese was not detected in most of samples except white Hard Salt Khewra.

Zinc (Zn)

Zinc is an important element performing a range of functions in the body, as it is a cofactor for a number of enzymes. It helps normal tissue functioning and is necessary for handling proteins and carbohydrates within the body. Zinc deficiency leads to growth failure and poor development of gonadal functions which can cause loss of taste and appetite, baldness, delayed wound healing, growth retardation, heart diseases, mental illness, delayed sexual maturity and reproductive dysfunction.

Lead (Pb)

Lead is retarded as high hazardous for plants and animals. Long term intake or exposure can result in a build of lead in the body and can cause more severe symptoms. These include anemia, pale skin; decrease handgrip strength, abdominal pain, nausea, vomiting and paralysis of the wrist joint, chances of miscarriage or birth defects [24]. Recommended dietary allowances (RDA) for Lead is less than 100 μ g / day. Thus results of all samples are in accordance with RDA value.

Chromium (Cr)

It is an essential micronutrient. Chromium poisoning results not from dietary sources but from industrial exposure. Chromium exposure has been connected with excess mortality from cancers of nasal cavities. The daily requirement of chromium is 0.002 g/ 70 Kg of body weight or 0.1 to 0.2 mg.

From the above results it is clear that Khallar and Kohat salt are the most impure salts containing higher contents of insoluble matter, magnessium, calcium and sulphate. So these salt need purification processes prior to use specially for food purposes and chemical industry. As pure salt passes quickly into the material to be preserved but the presence of magnesium chloride and calcium chloride delays the penetration.

Magnesium presence in Khallar salt in higher percent make it unsuitable to be used as such in electrolytic cells due to the fact that in the presence of excessive magnesium, hydrogen will evolve at the anode. Hydrogen and chlorine form an explosive mixture. Explosion in the cells or in the chlorine liquification may damage equipment and release chlorine to the environment. Chlorine gas is highly poisonous and dangerous. Impure brine in Mercury cells will cause butter formation. Butter will disturb mercury flow causing short circuits that burn the electrodes. Butter removal will expose workers to mercury vapours that are damaging to health. Disposal of mercury butter is costly and undesirable for the environment. In addition Magnesium on the surface of the salt crystals absorb humidity from air and makes the salt damp hence the salt loses market value.

In soda ash production excessive sulphate reduces the value of the product, using salt with higher sulphate percentage may lead to production loss. Accumulating calcium in the process causes encrustation. Periodical scale removal is costly and leads to loss of production. Therefore presence of

impurities in salt has serious economic, health and environmental consequences. Impurities increases the cost of brine treatment in chemical processes magnifies the problems of contaminated effluent disposal and necessitate costly refining of salt for human consumptions. Impurities in salt affect the food and chemical industry.

The metal load in all the samples are within safe limits, so there is no serious concern about heavy metals. Except Khallar and Kohat salt, all other salt samples do not need laborious purification methods. As many of the salt samples may be used directly for some chemical purposes, but with purification processes it can be converted into a valuable high quality food grade or B. P grade salt

Experimental

Chemicals used for analysis were of analytical reagent grade and used without further purification. Water used was distilled twice over alkaline $KMnO_4$ solution.

Sample preparation

The salt samples were crushed, sieved to – 80 meshes and stored in appropriate airtight glass container. Taken 1 g of each sample and dissolved in 100 ml doubly distilled water and separated the residue by filtration. Then volume of the filtrate was made up to 250 ml for further analysis as per ASTM method [16].

Atomic absorption spectrophotometer

The salt solutions were prepared by dissolving 5 grams of powdered sample in 10 ml of nitric acid and 90 ml of doubly distilled water in 100 ml of flasks. These solutions were heated to ensure complete dissolution of metal ions. Then trace elements were determined by using atomic absorption spectrophotometer (model # Z-8000 Hitachi, Japan).

Conclusions

As rock salt is used directly without any prior treatment in many areas of Pakistan so its quality parameters must be kept in mind for its safe human consumption. The impurities in the Kohat and Khallar salt must be removed prior to safe human consumption while Khewra salt may be used as such for food purposes. Due to the highest quality of lake salt and white crystal salt Khewra, these may be used for pharmaceutical preparations after treating it with pyrogen removing techniques. So it can save a lot of foreign exchange by manufacturing table salt and B.P grade salt locally from indigenous sources. The comparatively less pure salt of other deposits may be used for other chemical industries due to lower cost of the raw salt.

References

1. S. H. Faruqi *2nd National seminar on development of mineral resources*, Peshawar 21 (1983).
2. G. S. Alan, A. Hussain and Asrarullah, *Pakistan, Rec.Geo. Sur. Pak.* 40, 14 (1975).
3. G. S. Alan and Asrarullah, *Rec. Geo. Sur. Pak.*21 (1972).
4. Asrarulluh, *CENTO symposium Lahore.* 303 (1962).
5. Asrarullah, *Pak. Geog. Rev.*, **18**, 1 (1963).
6. W. A. K Christie, *Rec, G.S.I V*, 44 241 (1914).
7. A. B. Wynne, *Mem.Geo.Sur.India.*, **14**, 1 (1878).
8. M. H Khan, *Rec. Geo. Sur. Pak.*, **6** (1952).
9. E. R. Gee. The age of saline series of the Punjab and Kohat, *Proc. Nat. Acad. Sci. India.*, **14**, 269 (1944).
10. O. Farrar "The Dispensatory of United States of America 25th Edition (1955).
11. D. W. Kaufman, Sodium Chloride, New York, Reinhold, ACS Monograph No.145 (1960).
12. J. F. Van Oss "Materials and Technology" volume 1, *Air, Water, Inorganic chemicals and Nucleonics* (1968).
13. W. W. Scott and N. H. Furman, *Standard method of chemical Analysis.*, 1, 6th Edition (1962).
14. M. Artho and R. Kelly Analytical Chemistry. John Willey and Sons.Inc.New York (1998).
15. G. H. Jeffry, J. Basset, J. Mendhan and R. C Denney Vogels Text book of Quantitative Chemical Analysis.5th Edition Longman Group London (1994).
16. Annual book of ASTM standards E 534-98 Volume 15.05, Standard Text methods for chemical analysis of Sodium chloride p 519 (2002).
17. AOAC official method of analysis, 17th edition volume 1,Chapter 11, p31 (2000).
18. Codex Standards for food grade salt CX STAN 150-1985, Rev, 1-1997 Amend 1-1999, and Amend, 2-2001.
19. A. K. Pendias and H. Pendias, Trace elements in

soil and plants. Ist edition Boca Raton, F 1;CRC Press, 365 (1984).
20. A. Jacob and M. Worwood, "Bload and its disorders". R. M Hardesty and D. J weatherall. P 135 (1974).
21. D. Watson, Safety of chemicals in food, chemical contaminants, published by Ellis, NewYork, p 109 (1993).
22. K. A. Smith "Manganese and Cobalt in heavy metals in soil" Ed. Bj Alloway, Blackie. Glasgow, p 197 (1990).
23. E. U. Underwood, *J. Hum. Nutr* 35 (1981).
24. B. E. Davies "Lead in heavy metals in soil" Ed.Bj, Alloway.Blackie, Glasgow, p177 (1990).