Pilot Plant Study to Utilize Waste Brine Generated by Salt Industries

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Abstract: Since early 80s, people of Pakistan have been enjoying good quality of salt known as refined salt. Mechanical salt washing is used in many countries to upgrade salt quality. The counter current washing at multiple stages and dewatering by centrifuge improves salt quality. During this process almost 10 to 15% of salt is converted into saturated brine solution containing high amount of sodium chloride, calcium, magnesium, potassium and sulphate. In the current practice most of the salt processers, this brine waste solution is drained. In the present study, a method is modified to utilize this waste brine solution. Brine was treated with calcium oxide and iron chloride to remove some soluble and insoluble impurities. The treated brine is evaporated in a specially constructed jacketed crystallizer connected with a hot water geyser. Heat is transferred through bottom by counter current flow. The temperature is maintained between 55 to 65^{o}C at pH 3-4. The applied study yield the well shaped pyramidal crystals of salt known as Fluer de sel (flower of salt), that are world famous and used in gourmet foods with a growing market. Fleur de Sel has unique morphology, lower bulk density, large surface area, improved taste and rapid dissolution as compared to the common cubic salt

Keywords: Sodium chloride, waste brine, magnesium removal, temperature, pyramidal crystal.

1. INTRODUCTION

The impact of high salinity on environment especially on living being and metal is well known and many papers have been published on the same [1-3]. It is important to make the salt industry friendly to the environment, while utilizing salt, otherwise it could have a very adverse effect on the environment. Therefore, this high density brine salt waste should be processed so that at the end of the pipe-line, this industrial waste should not affect environment. Changes in the natural factors, no matter how minor, can have an enormous effect. Factors such as sunlight, pH balance and salinity challenge the survival of marine life on a daily basis [4].

To upgrade salt quality, mechanical salt washing is used in many countries. The counter current washing at different stages and dewatering by centrifuge upgrades salt quality from 94 - 99.4 %. The major impurities of salt like calcium, magnesium, potassium and sulphate are separated from salt in upgradation process. During this up gradation process 10 - 15% of salt is converted into saturated solution by dissolving in water and known as “waste brine”. All the excess brine drains into sewerage by almost all of salt processors and may cause harmful environmental effect on the living organism and sea life [5].

The current study deals the utilization of waste brine by converting it into environmental friendly solution and make value added product for utilization in food and industrial purposes [6]. Many reports are available in the literature to utilized waste brine [7-10]. Similarly, preparation of some value added products like, KCl with double effect vacuum evaporation, bromine extraction by distillation and production of $MgCl_2.6H_2O$ and $MgSO_4$ by mono effect evaporator were also published [10]. In the current study we have converted this waste brine into a salt known as Fluer de Sel, which is famous for its taste and unique crystal structure [11].

The up gradation of this improved quality of salt but the waste generated caused environmental pollution. The quality demand of industries has attracted the salt processers to introduce the same type of salt for different industries such as textile, soap, water softening, chloro-alkali and hundreds of many other applications. The washing process not only improves the whiteness of salt but also reduces the impurities of salt, like calcium, magnesium, potassium, sulphate and bromide [12]. Unfortunately instead of modern technique like re-crystallization for making the superior quality of salt like Pure Vacuum Dried, the mechanical water washing for upgrading the salt is very common in Pakistan especially in Sindh and Balochistan regions due to its low processing cost. However, the presence of impurities in salt has serious economic and environmental consequences [13]. In this region nearly twenty three salt processors are using mechanical refining process and producing approximately 28000 ton / month finished product (Figure **1**) [14].

The waste concentrated brine solution can be used as a source of many useful products which can also be

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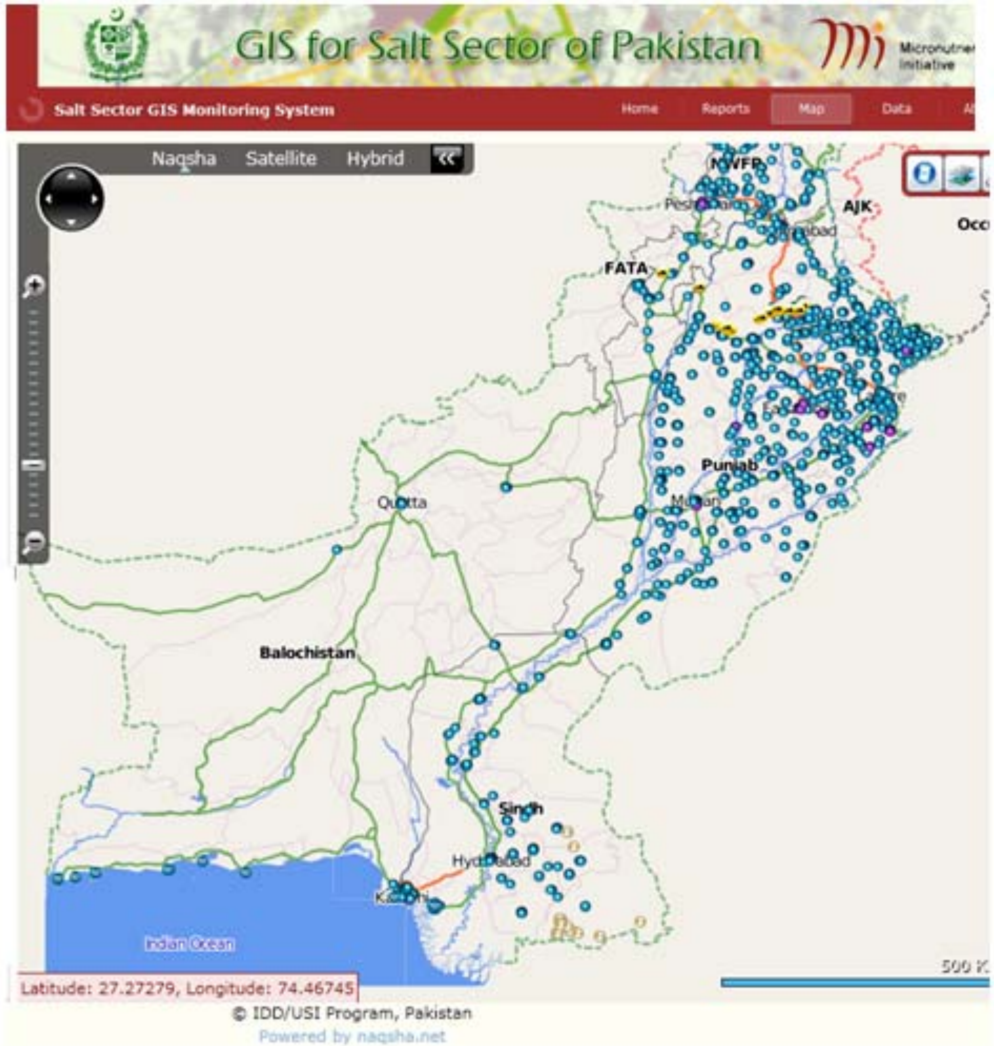

Figure 1: GIS Data for Salt Producers and Processors in Pakistan [14].

utilized after removing major impurities but unfortunately it is disposed off back into the sea without utilization [15-16]. This process causes an osmotic shock of the living organisms (ecosystems) in the sea. The effluent in the waste is a heavily concentrated brine solution. This discharged effluent has the potential to kill organisms. Although the brine solution containing natural ingredient of the sea water which may causes damage by unnatural concentration to marine population near outlet [4-5]. It is important to make the salt industry friendly to environment, because it could have very adverse effect on the environment.

2. PROCESS DESCRIPTION

2.1. Salt Refining Process

Raw salt is transported by truck from the harvesting area. The next stage is washing of salt with water in a conical tank by counter flow effect. Saturated brine having a density of 23^{o} Be (**Baumé**), the overflow of this tank is purged outside. The salt after washed is pumped as a slurry to the hydro-cyclones and then to dewatering conveyors which are followed by hydro mills to make the salt ready for the second washing stage. The second stage is similar to the first one with different washing brine which is cleaner than the previous brine. The last stage is the final dewatering by worm scroll type centrifuge to have a moisture content of maximum 4.0% by weight [17-19]. Some processors further use Rotary Dryer for drying the product upto 0.005% moisture.

3. MATERIAL AND METHODS

3.1. Collection of Samples

Waste brine samples were collected from different salt processing units situated in Sindh and Balochistan provinces of Pakistan. The sample collection was made

Table 1: Average Composition of Upgraded Salt in Pakistan

Salt / Ion	% Composition
NaCl	98-99.4
Ca^{2+}	0.07-0.2
Mg^{2+}	0.03-0.05
SO_4^{2-}	0.24-0.7
Br^-	0.0078-0.0095
K^+	0.0016-0.0030

Table 2: Average Composition Range of Waste Brine Effluents and NEQS Limit for Waste Water

Salt / Ions	Concentration mg/L= ppm	NEQS* mg/L= ppm
NaCl	250000-290000	1000
Ca^{2+}	1100-2100	---
Mg^{2+}	6000-11300	---
SO_4^{2-}	4300-10700	600
Br^-	30-100	---
K^+	320-960	---
TDS	264000-317000	3500

***National Environmental quality standards.

in cleaned and dried plastic cans. The collected brine was immediately transported to the laboratory for further chemical analysis and brine treatment. The samples were analyzed for their chemical composition of major salt impurities such as calcium, magnesium, sulphate, potassium and bromide and for the analysis of salt and brine samples standard procedures were used [22].

3.2. Pre-Treatment of Brine

During many previous experiments, influence of the concentration of magnesium ions on the crystal shape was observed. It was noted that high concentration may cause the formation of irregular pyramidal crystals and sometimes only crust formation was observed. The same phenomenon was reported by S. Inoue *et al.* [6].

Finally for the pretreatment of brine, precipitation of magnesium as magnesium hydroxide was performed to eliminate or decrease the concentration of magnesium ion from waste brine.

3.2.1. Removal of Magnesium

The waste brine was taken in a 150 L cylindrical tank. The amount of magnesium was calculated by analyzing the brine volumetrically. Calcium hydroxide was added to waste brine stoichiometrically, until the complete precipitation of magnesium as magnesium hydroxide. It was observed that some amount of calcium sulphate also precipitate due to common ion effect and limited solubility of calcium sulphate in brine [20]. Reaction was performed with gentle stirring, as vigorous stirring may increase the settling time of magnesium hydroxide [21]. Ferric chloride was utilized as coagulant to precipitate out all insoluble impurities. After analyzing and to ensure complete removal of magnesium from waste brine, six hours time was given to solution to be settled. All the impurities were settled down into the bottom and the clean and clear brine was transferred into another clean tank. Before and after brine treatment, brine was analyzed for its chemical composition (Table **3**). It was observed that in the absence of magnesium. The concentration of calcium is noticeably increased. A 106 L of brine was transferred for further crystallization.

Table 3: Composition of Waste Brine Before and After Treatment

Salt / Ion	Concentration Before processing mg/L=ppm	Concentration After processing mg/L=ppm
NaCl	276000	287000
Ca^{2+}	1840	3350
Mg^{2+}	5010	20
SO_4^{2-}	6220	4690
Br^-	42	41
K^+	380	387

3.2.2. Crystallization Method

During over previous work, we observed temperature impact on the well shaped pyramidal crystals. The Meta stable zone for the nucleation and crystal growth was observed between 55–65^{o}C. It was noted that direct heating from bottom may cause the irregular crystal growth, that was produced on uneven temperature in the same crystallizer and resulted formation of different crystallization zones. To overcome this fault, a small scale pilot project was designed for the utilization of waste brine.

For the crystallization of sodium chloride, 5x6 feet stainless steel (316L) jacketed crystallizer was designed which was attached with geyser though pipes and hot water was circulated for constant heat transfer (Figure **2**). Waste brine was filled in the open type crystallizer and temperature was maintained by circulating hot water inside the jacketed crystallizer. Temperature (55-65^{o}C) was adjusted by the geyser flame or controlled flow of circulating hot water. The observations were taken for the crystallization of square pyramidal crystals. Crystallized pyramidal crystals were collected and analyzed for their chemical compositions thrice (Table **5**) noted as S1,S2 and S3. The brine solution was also analyzed throughout the experiment. Fresh brine was fed from the bottom corner of crystallizer to maintain brine level in crystallizer.

Table 4: Surface Area (Specification) of Crystallizer Used for Crystallization

Item	Measurement
Total surface Area of crystallization section	2.787 m^2
Depth of crystallizer	50 mm
Thickness of sheet	1 mm

Figure 2: Especially Designed Jacketed Crystallizer for Pyramidal Crystals.

4. RESULTS AND DISCUSSION

At the starting point, the level of brine was 25 mm in the crystallizer and temperature was maintained at 58^{o}C. No crystals were observed. As the initial super-saturation was obtained, few small nuclei were observed. As a result of gentle evaporation of water and subsequent reduction of volume, more nuclei started to generate and demonstrated 3 mm width of the base while few crystals sank to the bottom of the crystallizer. During the crystallization process, the level of brine in the crystallizer was maintained between 23-25 mm (Figure **3**). Samples of brine were collected and analyzed for calcium, magnesium, potassium, bromide, sulphate and sodium chloride contents. Table **6** shows result of brine at different stage as B1,B2 and B3.

Figure 3: Well Shaped Pyramidal Crystals formation by Waste Brine.

The temperature was maintained at 60^{o}C but at the time to collect crystals and as a result of fresh brine addition temperature decreased slightly but during the whole experiment it was maintained in the range of 55-60^{o}C. Temperature was controlled by maintaining the flow of circulation water in jacketed wall of crystallizer or by adjusting the flame of geyser. Formation of large numbers of tiny nuclei was observed as a result of agitation during collection of crystals. Once the unstable crystallization zone was created, the system lost its meta-stable region. Agitation in any reason was observed as the formation of irregular morphology of crystals. Crystals grow on the surface as invert square pyramidal shape. Brine composition, pH, temperature and static environment were the key factors to controlled crystallization. In general the pyramidal crystals can be crystallized by the bittern of salt industries but due to high level of impurities like magnesium and sulphate which decreases the solubility of calcium in brine is the main reason of formation of irregular morphology. The solubility of calcium sulphate in brine increased with the increase in

Figure 4: Irregular crystal formation result high magnesium content brine.

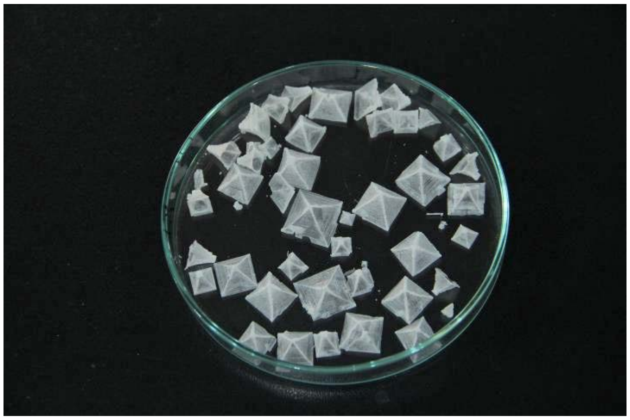

Figure 5: Well shaped Pyramidal Crystals.

the sodium chloride concentration [7]. Additional experiments were also performed to study the crystallization because since the presence of high level of sulphate and magnesium in meta-stable zone disturbed resulting crystallization of pyramid in the form of discontinued or irregular morphologies as shown in Figure **4**. Some well shaped pyramidal crystals can be seen in Figure **5** and Table **5** shows chemical analysis of pyramidal crystals. Figure **6** shows the scan electron microscope (SEM) view of a single pyramidal crystal.

X-Ray Powder Diffraction (XRD)

Crystallized pyramidal crystals were analyzed on XRD powder diffraction. The x-ray diffraction (XRD) pattern of pyramidal crystals sample was obtained using X-ray diffractometer at 40 kV, 40 mA and scanning rate of 2^o / min over a range of 5 -70 2. XRD pattern confirms that crystallized pyramids are sodium chloride. Figure **7** represents XRD pattern for sodium chloride.

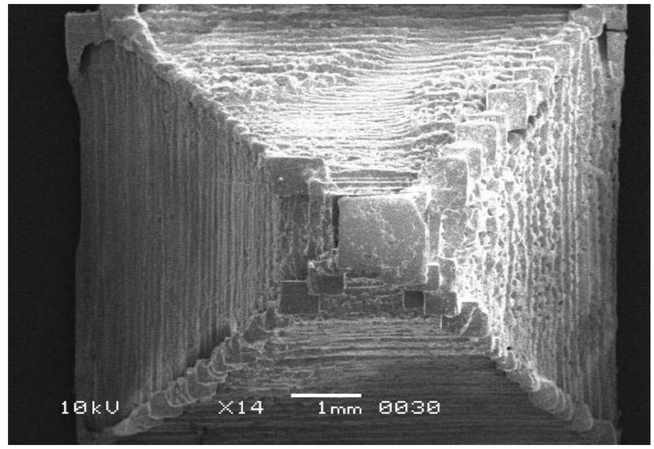

Figure 6: SEM view of Pyramidal crystals of NaCl.

5. CONCLUSION

This study developed a new methodology to utilized salt industrial waste brine. This ensures stable crystallization of regular pyramidal crystals of NaCl from waste brine. Removal of magnesium as

Table 5: Chemical Composition of Pyramidal Crystals

Chemical Elements	Result (%) S1	Result (%) S2	Result (%) S3
Sodium Chloride	98.1	97.6	97.15
Sulphate	0.74	0.85	0.975
Calcium	0.24	0216	0.264
* Magnesium	N.D	N.D	N.D
Potassium	0.053	0.048	0.0104
Bromide	0.0080	0.0038	0.0064

*N.D not detected by volumetric method of complex metric titration.

Table 6: Chemical Composition of Brine Solution During Experiment

Chemical Elements	Result mg/L=ppm B1	Result mg/L=ppm B2	Result mg/L=ppm B3
Sodium Chloride	304000	312000	323000
Sulphate	4930	5410	6310
Calcium	3110	2520	2300
Magnesium	24	30	48
Potassium	380	408	470
Bromide	51	56	54

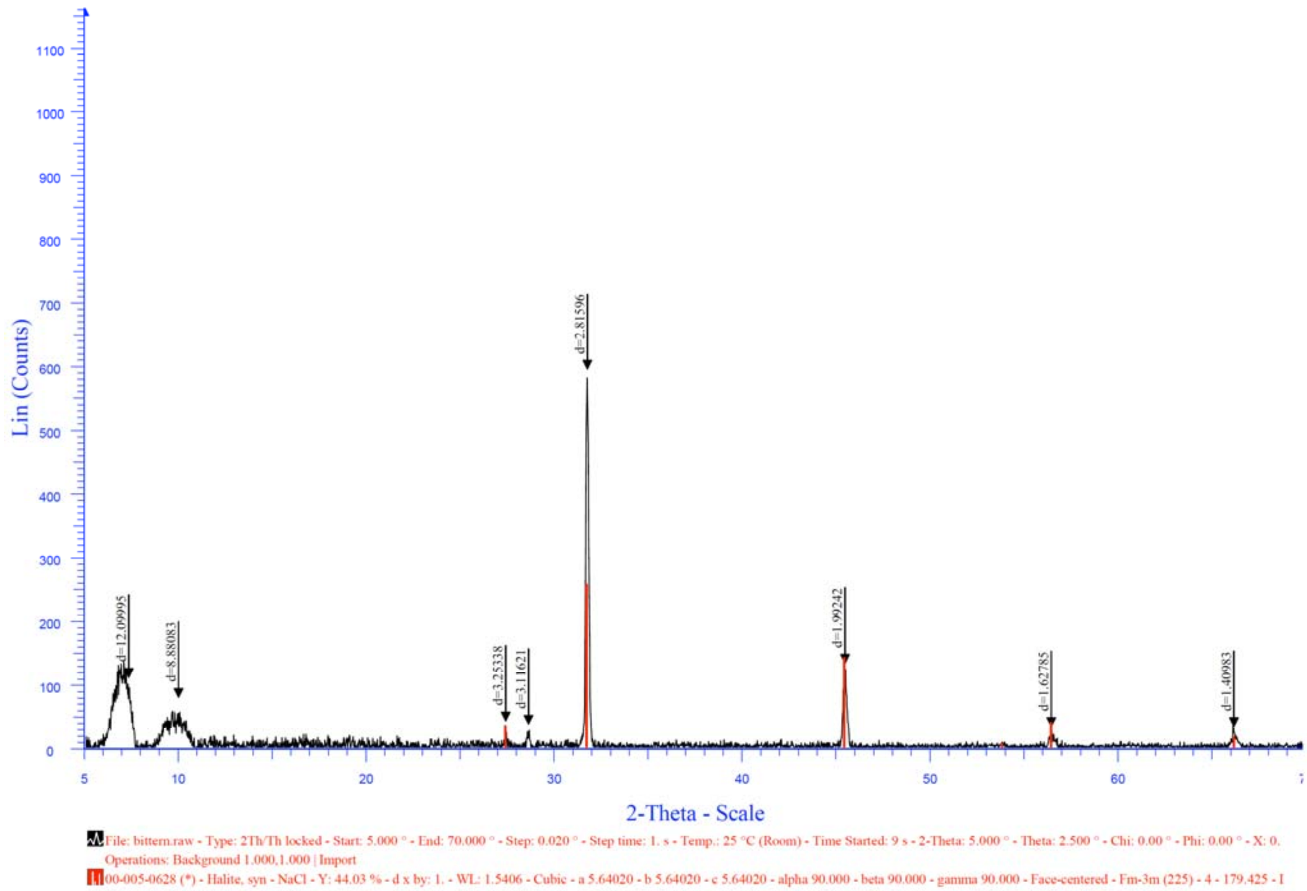

Figure 7: XRD Pattern of Crystallize Pyramids of NaCl.

magnesium hydroxide was noted as a key factor to avoid the hindrance of magnesium during crystallization process. The temperature ranges between 55-60°C and pH between 3–4 was found to be optimum for crystallization of regular pyramidal crystals from waste brine.

The crystallized pyramidal crystals gave a new idea to convert worthless and waste brine into a value added product. Pyramidal crystals formed have different properties from those of cubic salt, like rapid dissolution and improve taste. Growing international market for pyramid salt, have led to the manufacture and commercial availability of this salt in Pakistan.

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