BIOMINERALIZATION: A SAFER ENVIRONMENTAL AND INDUSTRIAL BIOFILTER APPLICATION, EMISAL Co. CASE, EGYPT

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EXTENDED ABSTRACT

Economic feasibility of extracting salts from Lake Quaroun resembled the requirements for environmental re-balancing of the continuously increasing salinity of the lake water and to conserve its bio-diversity populations. Industrial salt extraction of anhydrous sodium sulfate started by 1993 through brine concentration route via four successive concentration ponds.

Extracting the anhydrous sodium sulfate was achieved through pumping the brine of 336 g/l ± 15 g/l to the plant as a requirement to nucleate glauber salt. Brine specifications of Ca^{+2} content as not more than 200 ppm is a key-turn as to avoid building of scales in both the heat exchanger and the crystallizer units. The Ca^{2+} content reaches about 300 ppm it causes losses of 4 hours/day of the plant working time for melting and de-scaling the precipitated Ca^{2+} as gypsum.

Proper pond management of the flowing brines and Biomineralization of blue-green and violet algae types succeeded as a bio-filter to mineralize the algal species turning it into algal mats deposited at the bottom and forming a thin calcrete band. The Ca^{+2} content did drop to average range between 170-190 ppm causing reduction of required time for de-scaling by half. The process proved its efficiency through maintaining constant flow regime and algal population densities in pond no.2, where salinities matches calcium carbonate precipitation, formulates the requirements for consistent regime performance.
The applied process of biomineralization proved its efficiency as a safer environmental approach on industrial scale. The beneficiary economic goals since 1996 till the end of 2004 resemble gaining 6500 hours of production. The main goal encloses the direct application of bio-filter concept as a re-cycling of industrializing brines.

Keywords: Lake Quaroun – concentration ponds – biomineralization – osmosis pressure – Ca content – scales – production hours.

INTRODUCTION AND SCOPE

Lake Quaroun (Fig. 1) represents efficient part of Egyptian history, where its potential economic resources were based on the fact of its fertile land for cultivation and fish resources. Last two centuries witnessed deterioration events raised by damming and bridges over the Nile course hindering excess floodwaters from reaching the depression through Yossef canal as described by Beadnell (1905). The main results appear in raising the salinity in Quaroun Lake water during the 18th century (Said, 1981). The raising rate witnesses few turns since then (10.5 g/L in 1906 till 35.3 g/L by 1976), but the outcome by the beginning of the 19th century focused first on the bio-diversity changes in the fish population. This result changing the aqua population into marine ones by 1928 to adapt the continuous rise in salinity till it matches the seawater salinity 33± 2g/L (Fig. 2) and since then biodiversity in fish population and types had started (El-Shabrawy, 2002). The anticipated view summaries the pessimistic view (Fig. 2), which urged scientist to interfere and to propose way outs taking into consideration the environmental balances between living and non-living natural resources. This fact was exaggerated due to the fact that Lake water level was 70 m a.s.l. (Above sea level) and dropped to -43.80 m b.s.l. (below sea level) according to the study carried out by FWMP, 1999 and 2000 (Fayoum water management project). Consequently, stabilizing the lake water level at –43.8 m b.s.l. ± 0.6 m is another challenge to limit salinity rise. Ministry of irrigation and water resources in collaboration with Ministry of agriculture approved adding agricultural wastewaters into the lake as to stabilize its level and to control its salinity gradient rise.

During the seventies, trials to estimate the economic beneficiation of salt extraction as a clue to re-balance and/or turn back the situation in the Quaroun Lake into norm was the target heading to re-directing thoughts for a better sustainable development of the area as a whole. Implementation to extract salt was a convincing concept by Ministry of Industry; hence studies were devoted to El Nasr Saline Co. (ENSCO) to carryout the project. ENSCO started in collaboration with the British White Young and Partners by 1976 and their final study reached its goal by 1979, where DSS engineers INC Coopers and Lybrand CRS International final report was approved. The feasibility study indicates possible economic extraction of Na_2SO_4, NaCl and Mg salts from Lake Quaroun water. The three products proved to be of ultimate need to replace imports and to satisfy local domestic and industrial market.

SALT EXTRACTION AND SCALE FORMATION

Since the execution of the approved feasibility study, the Egyptian Salts and Minerals Co. (EMISAL) was the founder of this step as industrial complex site with three main targets, these are:
1-Extraction of economic salts from Lake Quaroun water to control salinity rise.
2-Establishing industrial base in Fayoum region with expertise in salt industry.
3-Increasing economic income through replacing imported product and to satisfy local market with possibility for export.

The Egyptian Salts and Minerals Co. started production by October 1992 (Dardir, 2000 and 2002a) with a designed capacity of 100 000 tones per year of high quality anhydrous sodium sulfate. Infra structure of the site required 3 years of continuous work to cut-off the design area (Fig. 1) in order to subdivide part of the area into four evaporation ponds with a dyke separating the battery limit from Lake Quaroun. Lake water are pumped to the evaporation ponds (ponds 1- 4, Fig. 1), where concentration reaches 340 g/L in average as to suite the crystallization of glauber salt by cooling and then drying-up will led to anhydrous sodium sulfate product.

The previously mentioned amounts formulate effective parameter as to control salinity increase of Lake Quaroun water. The salinity at the year 2010 was estimated to reach 40 g/l. The recorded measures indicate lowering of average salinity measures during the last 5 years to reach 34-35.5 g/l meaning a lowering of 4-5 g/l than the previously estimated measures (Fig. 2). This result was reached through direct cooperation between the Ministry of Water Resources and Irrigation and the company (EMISAL).

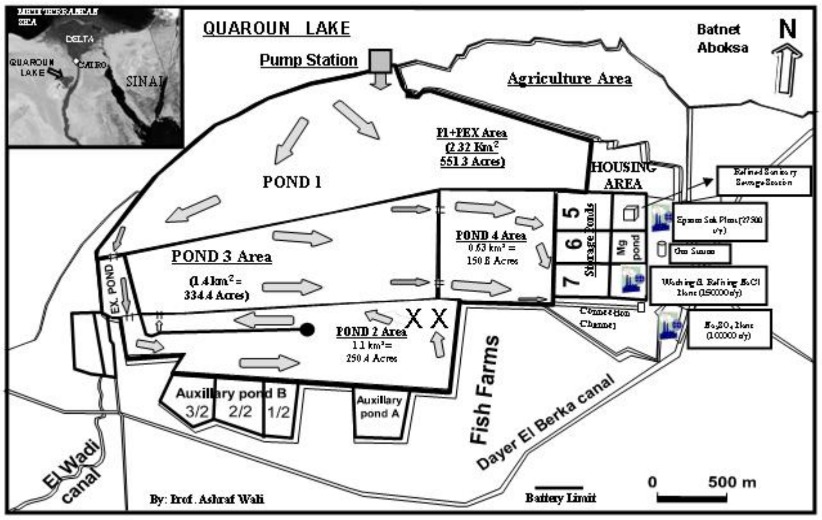

Figure 1: Layout map of the Egyptian Salts and Minerals Co. (EMISAL) showing the concentration ponds

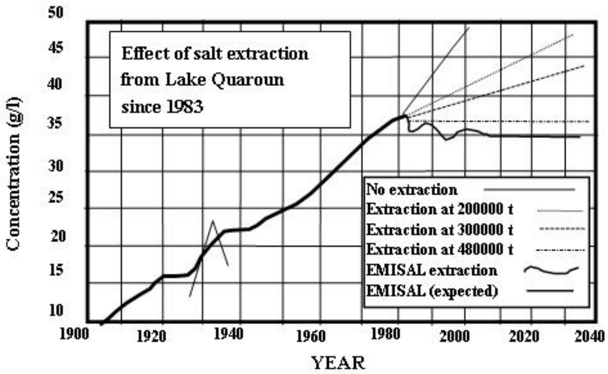

Figure 2: Salinity increase relation with time and the anticipated decrease with salt extraction from Lake Quaroun

The amount of calcium in the Lake Quaroun water composition did represent a serious problem through industrializing the concentrated brine out of concentration pond no. 4. The postulated design of the brine chemistry shouldn't exceed 200 ppm for calcium content otherwise the rate of scales formation will be accelerated and will block both the heat exchangers and crystallizers (Fig. 3) enforcing the production line to hinder until scale removal process ends. Table 1 summarizes the chemical composition of Lake Quaroun water indicating that the Ca^{2+} content fluctuate between 0.5 – 0.54 (wt%) covering the period between (1994 - 2004). The pass way of the flowing brine started from pond no. 1 till pond no. 4 will lower the concentration of Ca^{2+} in the brine due to continual evaporation of the brine by solar energy. But at the out-let from pond 4 to the sodium sulfate factory, but the Ca^{2+} content was never below the limit i.e. < 200 ppm.

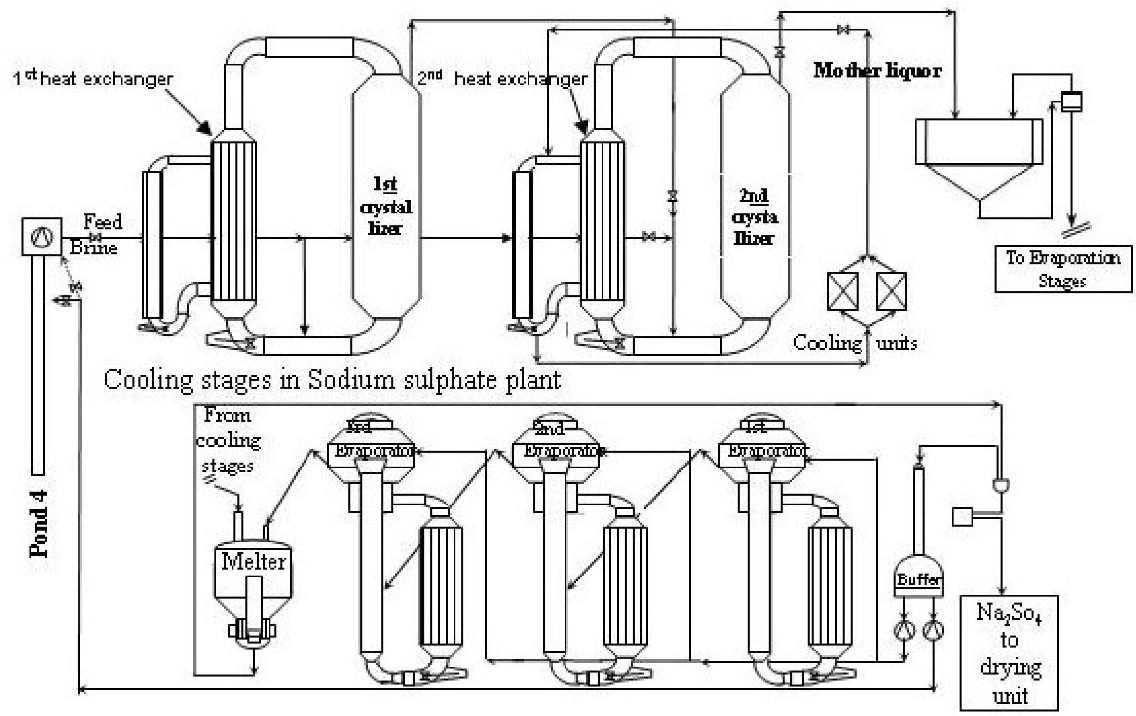

Fig. 3 General flow diagram of thenardite factory showing the cooling and hot sectors

BIOMINERALIZATION AS RECYCLED BIO-FILTER

The reduction of Ca^{2+} content will offer more production hours offering more profit to the company (tonnage amounts) as a direct goal, while excess energy cost for melting the formed scales by heating will represent an add value. Trials for lowering down the Ca^{2+} content value did cover a wide range discussing the possible of chemical buffer media forming a precipitates of calcium and then re-filtering. These trials in addition to its coast didn't proof its practicality and would causes unpredictable complications that may cause changes in the chemical composition and in the brine-alloy interaction inside the factory units.

Table 1: Average chemical composition of Lake Quaroun water (1994-2004)

Year	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**
Sp. Gr. gm/cm^3	1.024	1.026	1.028	1.028	1.027	1.026	1.026	1.023	1.023	1.023	1.027
TDS (g/l)	34.9	35.4	36.7	37.2	35.3	35.6	35.9	33.3	33.9	34.	36.1
CO_3^{2-}	0.034	0.030	0.031	0.023	0.03	0.029	0.027	0.024	0.026	0.028	0.025
HCO_3^-	0.48	0.39	0.38	0.35	0.355	0.315	0.32	0.341	0.339	0.333	0.383
SO_4^{2-}	8.89	9.1	9.12	9.65	9.35	9.44	9.45	8.80	8.74	8.73	9.89
Cl^-	14.2	14.1	14.2	13.89	13.04	13.17	13.23	12.52	12.74	12.87	13.0
Ca^{2+}	**0.5**	**0.51**	**0.52**	**0.396**	**0.492**	**0.484**	**0.494**	**0.455**	**0.495**	**0.499**	**0.501**
Mg^{2+}	1.31	1.32	1.36	1.411	1.365	1.312	1.293	1.253	1.246	1.225	1.219
Na^+	10.52	10.6	10.9	10.53	9.94	10.15	10.22	9.53	9.72	9.77	10.41

The preliminary thoughts about adapting biomineralization as a concept in brines for industrial applications was leaded by Prof. A. Wali and some of his co-workers e.g. Wali (2000) and Wali et. al. (1996 and 1997). The trials and recorded observations reveal the positive implication and implementation of a group of blue-green and violet algae to flourish within the salinity of the concentration pond no. 2 (Fig. 1). The main concept was based on providing the requirements as to flourish these species in the designed brine salinity range (95 - 110 g/l). The succeeding positive criterion concerns the effectiveness of the pressure difference between brine concentration and the nuclei leading to mineralizing the bio-cell itself and turning its composition into pseudo-hexagonal aragonite (Photo 1) as confirmed by microscopic examination and XRD lines. A more supportive view was achieved through the examined samples by SEM where a well crystalline pseudo-hexagonal crystal and their daughters can be detected easily (Photo 2). The role of bio-influence was farther approved through recording of the bio-capsule (Photo 3), where algal filaments encloses the mineralized nuclei, while upon heating by the dispersive beam, the decayed and captured organic gases are outburst causing rupture of the bio-capsule wall (Photo 4).

The main quarry was whether the bio-masses will fit the required passing volume of brine coming from pond 1 to pond 3 through pond 2 or not?. This challenge will render the process to grade up to true industrial bio-filter. Accordingly choice of the proper site for plantation was of prime concern as to fulfill the following variants:

1- Calm part to avoid wind effect as disintegration agent.
2- Suitable T.D.S range as to keep the planted species in flourishment.

Photos 5 and 6 represent two successive and demonstrative stages during the executing stages as above mentioned. Photo 5 represent a clear clue towards the successive flourishing generation of the bio-masses supporting the efficiency of the process. Mineralized genera are seen darker than the newly growing ones indicating the re-cyclicity of the bio-filter media. Photo 6 represents the dense plantation of the flourished species as a supportive tool for the capability of theses species to act as industrial bio-filter.

ACHIEVEMENTS, RESULTS AND SUSTAINABLE DEVELOPMENTS

The above mentioned process lasts for almost 16 month between trials and modifications until supportive figures were in hand. The Ca^{2+} content in the feeding brine show remarkable difference (< 200 ppm) starting by 1995 (Table 2).Continuous monitoring covering the exhausted volumes of brine within both 1st and 2nd crystallizers between successive two melts were closely recorded and the beginning of 1999 for the first crystallizer and at 2000 for the second crystallizer (Table 3). Figure 4 represent the relation between Ca^{2+} content in the feeding brine to the sodium sulfate factory, where a general decreasing trend was reached indicating continual decrease in Ca^{2+} content. Figure 5 represent the relation between the consumed brine volumes in both 1st and 2nd crystallizers with demonstrative increase in trend indicating increase in consumption volumes of brines continuously till 2003. A reduction in melting time was successfully reaching 1 to 2 hours constituting 25% up to almost 40% of the previous estimates for required daily melting time.

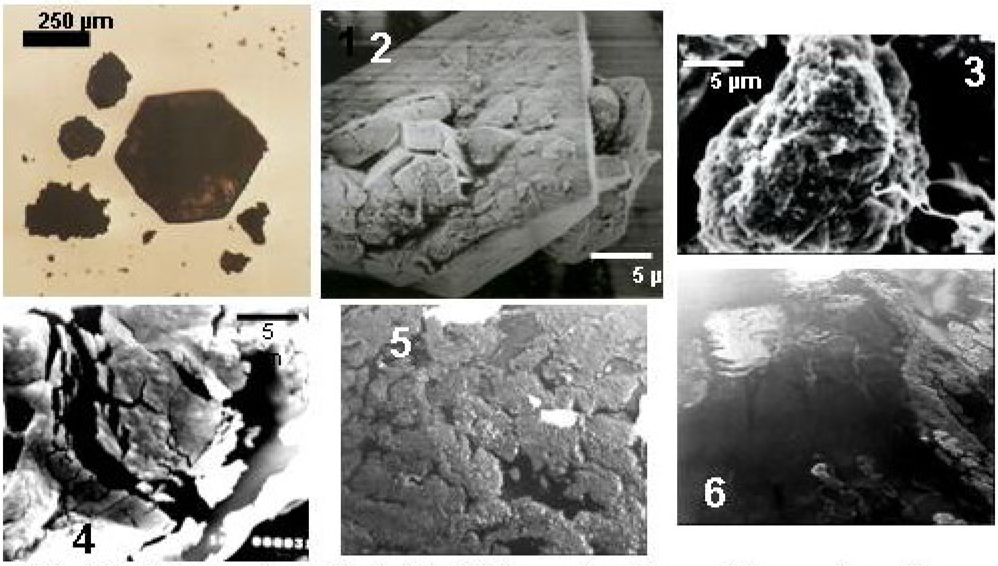

Photo 1: Pseudo-hexagonal aragonite, Photo 2: SEM close-up view of the pseudo-hexagonal aragonite, Photo 3: Bio-capsule, Photo 4: Rupture in bio-capsule, Photo 5: Blue-green algal bio-masses as a bio-filter and Photo 6: Blue-green and violet algae dense masses as a bio-filter for the brine in pond 2.

Table 2 Ca content (ppm) in the feeding brine to factory during (1994-2003)

Year	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Ca^{2+}	0.215	0.146	0.163	0.181	0.196	0.150	0.159	0.171	0.183	0.200

Table 3: Amount of feeding brine (m^3) between two melts (1st and 2nd crystallizers) during 1995-2003

Year	1995	1996	1997	1998	1999	2000	2001	2002	2003
1^{st} crystallizer	2148	1580	1737	1392	2185	2265	2542	2762	2945
2^{nd} crystallizer	3145	3043	3145	3168	3035	3530	3256	3188	3401

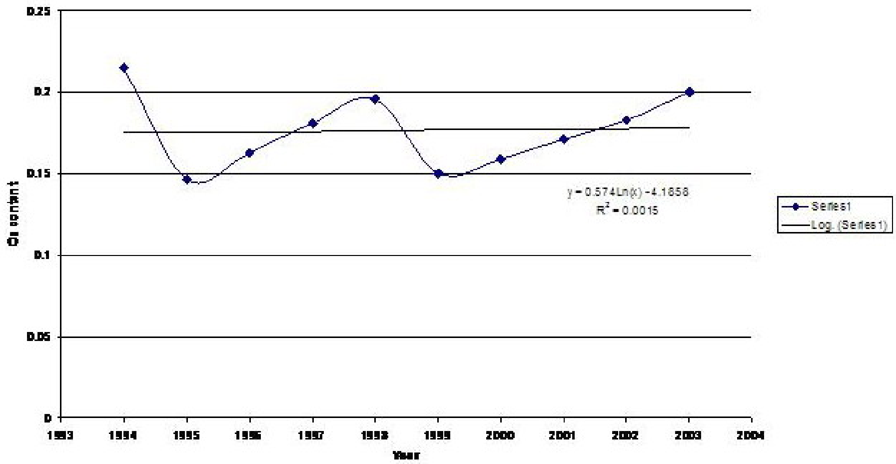

Figure 4: Relation between Ca2+ during the years with a mean trend

The Egyptian Salts and Minerals Co. (EMISAL) were founded as an environmental project with aim of extracting economic salts from the lake to minimize the annually added quantities. This aim will control events that could cause environmental hazardous

(Dardir, 2002b). Raising rate of salinity will turn the lake into second example as the Dead Sea, but the effect will farther threaten the social and welfare of the long lasting jobs as fishermen (about 10 000 in number). Continual efforts seemingly will never stop, hence the executed managing program of the lake by FWMP (2000) did record a step towards controlling the lake water salinity, but the added volumes of agriculture wastewaters did change the lake water chemistry (inorganic and organic constituents) enforcing the EMISAL expertise as to continually re-balancing the effects of the added components.

Lake Quaroun requires continuous monitoring as to predict and to control the migrating dune and adjust the lake water composition “organic content-type of added salts-bathymetry of the lake”. These parameters will offer safe preservation and protection of one of the oldest lake all over the world since its historical heritage and natural resources should be under sustainable development programs in order to maintain its continuous development

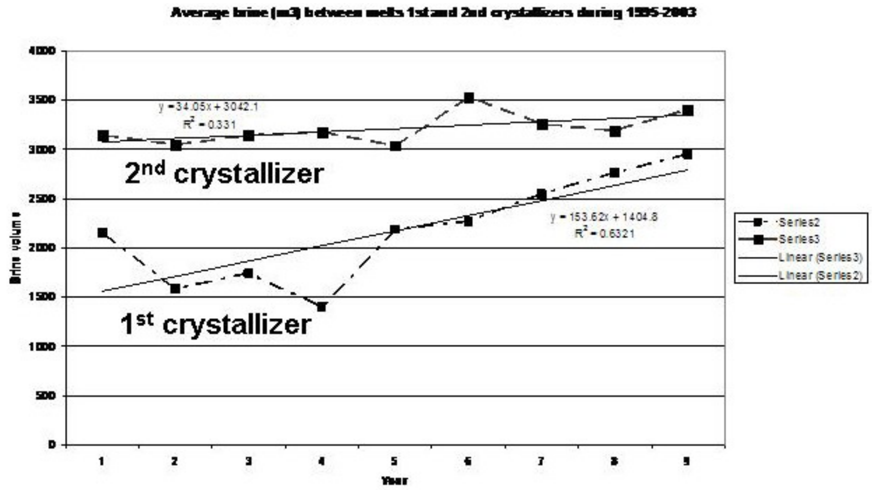

Figure 5: Average brine (m3) between successive melts

CONCLUSIVE REMARKS

A bio-mineralization concept was successfully applied on industrial scale covering a huge area (pond no. 2=1.1 km^2, Fig. 1), where the living cells were mineralized and produced aragonite ($CaCO_3$) as well crystalline pseudo-hexagonal crystals. Successive generation of the adopted genera did proof their capabilities to continual flourishing re-cycling as to indicate their success as a bio-filter. An increase in production time was scored by about 25% up to 40% of the required melting time. Biomineralization as a bio-filter proofs its efficiency on industrial scale with a pronounced achievement within the re-cycling frames. A more new proved phenomenon concerns the formation of “calcrete soil” formed of the mineralized few millimertric scale formed at the bottom of pond 2.

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