

PRODUCTION OF MARINE CHEMICALS IN PAKISTAN Part I. Sea Salt and Deterioration of its Quality

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Production of sea salt by solar evaporation has been described with respect to the physical conditions prevailing on the coastline, capacity and location of salt works and methods adopted for salt crystallization. The factors contributing to the deterioration of the sea salt industry and of the quality of salt produced there from have been described. The effect of untreated sewage and industrial effluents discharged through Lyari River into Manora channel on the salt works has also been assessed.

INTRODUCTION

Production of sea salt by solar evaporation is one of the oldest industrial activities. However, in Pakistan the continuous process of sea water evaporation and crystallization in solar ponds dates back to the 1970's. Natural factors like the geographical and weather conditions, particularly of the south east coastline of this country are ideally suited for locating salt works in this region. About a dozen salt works have accordingly been producing more than 500 kilo tons of salt per annum in and around the City of Karachi. The location and capacity of these salt works are listed in Table 1 [1].

The salt works have been in operation for over sixty years but their method is still primitive. There has been little improvement, if any, since that time and the industry continues to be both space and labour intensive. Neither measures of quality control have been adopted nor are the modern techniques of harvesting, storage and packing existent. Utilisation of by-products, *viz*, gypsum and bittern, has received no attention. Discharge of sewage and industrial effluents into Manora channel and Gizri Creek where the salt works are located leads to the admixture with their input and contributes to further deterioration of the quality of salt. The salt works, although they are sufficiently large, do not operate at their full/installed capacity and because of the low quality it finds only 30 % of the salt market in the country. The bulk requirement is met from raw salt transported from mines located in the Salt Range in the North.

It is being increasingly felt that production of good quality sea salt alone can create a local demand for it, otherwise, rock salt will have to be transported from the North, thus making the availability of this commodity

energy intensive. The overall condition of the sea salt industry in the country is critical. It has been depleted of its infrastructure facilities, there has been no balancing or upranking ever since its inception. It is now technically obsolete and is gradually deteriorating and sliding towards economic annihilation.

This paper describes the physical conditions prevailing on the coastline and effects of environmental degradation on the quality of solar pond input as well as the salt itself. It identifies the factors contributing to the deterioration of the quality of sea salt produced by the salt works.

METHODOLOGY

Samples of salt were collected from the local market as well as the salt works. Their analysis appears in Table 7. Sea water and brine samples at the various stages of crystallisation were collected from salt works. Detailed analysis of brine samples and the calculated concentration of various salts are presented in Tables 3 and 4 respectively.

RESULTS AND DISCUSSIONS

Physical condition and salt crystallization. Most of the salt works, as would be noted from Fig. 1, lie within a few miles of Karachi. The coastline on which they are located is characterised by bays, creeks, shallow water inlets and salt water marshes which are well suited to this industry.

The average relative humidity for Karachi varies between 50 % and 55 % from January to March, between 70 % and 80 % from May to October and 55 % to 65 % during November, December and April [2]. The correspon-

Table 1. Capacity and location of sea salt works in Karachi. (Latitude 24° 50' N, Longitude 67° 03'E)

Location Groups (In order from west to east)

| | Mauripur Coast | Korangi Creek | Gharo Creek | Capacity | Capacity range | Capacity Group |
|--|----------------|---------------|---------------|---------------|------------------------|----------------|
| | Kilo-ton/year | Kilo-ton/year | Kilo-ton/year | Kilo-ton/year | Kilo-ton/year | |
| 1. Khurshid Salt Works Ltd. | 130 | | | 130 | | |
| 2. Hirjina Salt and Chemicals (Pak) Ltd. | | | 110 | 110 | 110-130 | I |
| 3. Grax Limited | 45 | | | 45 | | |
| 4. Qureshi Salt Works | | | 40 | 40 | | |
| 5. Abro Salt and Chemical Works | | 40 | | 40 | 40-- 45 | II |
| 6. Dhabheji Salt Works Ltd. | | | 40 | 40 | | |
| 7. Laxmi Salt Works Ltd. | 15 | | | 15 | | |
| 8. Nausserwanjee Salt Works | 15 | | | 15 | 10-15 | III |
| 9. Gulbai Salt Works | 15 | | | 15 | | |
| 10. Sind Salt Works | | 10 | | 10 | | |
| 11. Mohammadi Salt Works | | | 10 | 10 | Inoperative since 1968 | |
| 12. Jhangra Salt Works | | 5 | | 5 | Inoperative since 1972 | |
| Total Capacity: | 220 | 55 | 200 | 475 | | |

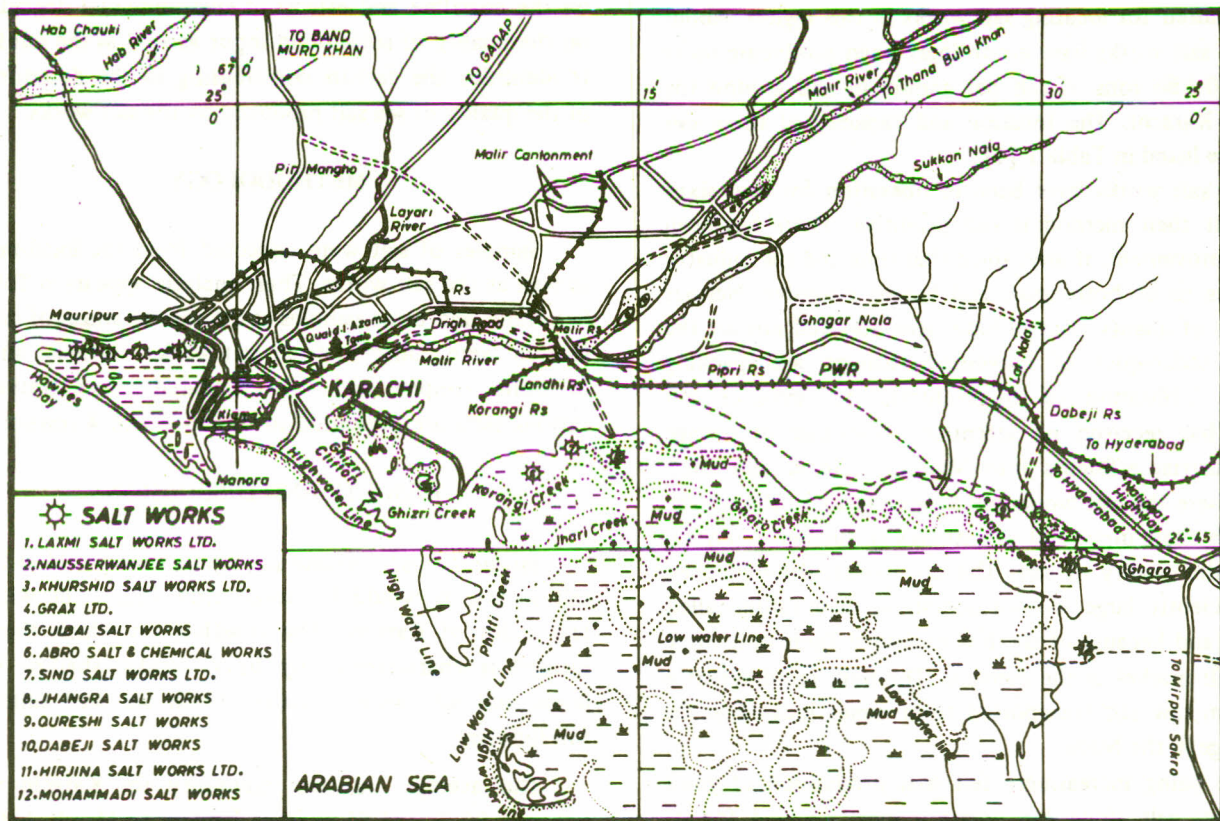


Figure 1. Sea salt works around Karachi

Table 2. Analysis of raw salt

| Raw Salt | Percent on dry basis | | | | | | | |
|-------------------|----------------------|------|------|------|------|-------|------|------|
| | (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) |
| NaCl | 91.33 | 89.2 | 92.8 | 95.2 | 92.0 | 92.56 | 93.6 | 92.2 |
| KCl | 0.52 | 0.85 | 0.51 | 0.35 | 0.38 | 0.45 | 0.43 | 0.52 |
| CaSO ₄ | 1.34 | 1.36 | 1.2 | 0.86 | 1.35 | 1.14 | 0.92 | 1.24 |
| MgSO ₄ | 1.94 | 2.15 | 1.19 | 0.97 | 1.62 | 1.82 | 2.01 | 1.33 |
| MgCl ₂ | 4.13 | 5.56 | 3.4 | 1.59 | 3.86 | 3.64 | 2.62 | 4.0 |
| Insolubles | 0.71 | 0.8 | 0.62 | 0.55 | 0.48 | 0.35 | 0.3 | 0.5 |

Table 3. Analysis of brines from different salt works

| Items | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|--|---------------------------|-------------------------|---------------|----------------------------|------------------|------------------|-----------------------------|---------------------------|----------------------------|--------------------------|--------------------------|
| | Salt | Salt | Salt | Salt | Salt | Salt | Salt | Salt | Salt | Salt | Salt |
| | Work-I Coastal Pump | Work-I Pump No. 1 | Work-I Pan | Work-II Coastal Pump | Work-II Pan 1 | Work-II Pan 2 | Work-III Coastal Pump | Work-III Pump No. 1 | Work-IV Coastal Pump | Work-IV Pump No. 1 | Work-IV Pump No. 2 |
| 1. pH | 7.1 | 8.5 | 8.5 | 7.0 | 8.5 | 9.0 | 8.0 | 8.5 | 8.0 | 8.5 | 9.0 |
| 2. Temperature (C) | 28.5 | 28.5 | 35.5 | 29.5 | 29.5 | 35.5 | 29.5 | 30.0 | 32.0 | 36.0 | 36.0 |
| 3. Density | 1.027 | 1.139 | 1.276 | 1.020 | 1.095 | 1.169 | 1.037 | 1.202 | 1.030 | 1.069 | 1.241 |
| 4. Putrescibility | Pass | 7 days Fails | Pass | Pass | Pass | 5 days Fails | Pass | Pass | Pass | 3 hrs Fails | Pass |
| 5. Total halides as Cl ⁻ (ppm) | 23049 | 116131 | 186165 | 24822 | 76239 | 128545 | 31914 | 157797 | 26595 | 54963 | 184392 |
| 6. Sulphate (ppm) | 3337 | 13647 | 21854 | 3029 | 10931 | 34543 | 4321 | 21220 | 3436 | 7807 | 35794 |
| 7. Total dissolved Solids (TDS, ppm) | 46252 | 232004 | 484580 | 46156 | 156000 | 317140 | 60068 | 402808 | 49700 | 110810 | 463300 |
| 8. Organic matter in TDS (%) | 15.9 | 17.2 | 42.1 | 15.5 | 18.6 | 34.5 | 16.9 | 34.9 | 13.6 | 17.3 | 31.0 |
| 9. Total hardness as CaCO ₃ (ppm) | 8000 | 33000 | 204000 | 8500 | 25000 | 86000 | 10000 | 88000 | 8000 | 22000 | 109000 |
| 10. Total alkalinity CaCO ₃ (ppm) | 500 | 500 | 2000 | 500 | 500 | 750 | 500 | 1000 | 500 | 500 | 1000 |
| 11. Permanganate No. mg O ₂ /Litr. | 123 | 150 | 210 | 132 | 185 | 260 | 133 | 465 | 290 | 310 | 470 |
| 12. Calcium (ppm) | 400 | 1603 | 601 | 400 | 1202 | 801 | 400 | 601 | 400 | 801 | 400 |
| 13. Magnesium (ppm) | 1702 | 7052 | 20550 | 1824 | 5350 | 20915 | 2188 | 20550 | 2188 | 4742 | 26265 |
| 14. Sodium (ppm) | 12000 | 56000 | 43000 | 12000 | 38000 | 46000 | 16000 | 59000 | 13000 | 29000 | 72000 |
| 15. Potassium (ppm) | 1000 | 3000 | 17000 | 1000 | 2000 | 7000 | 1000 | 8000 | 1000 | 2000 | 10000 |
| 16. Bicarbonates (ppm) | 610 | 610 | 2440 | 610 | 610 | 915 | 610 | 1220 | 610 | 610 | 1220 |

ding vapour pressure is 14-20 mm from November to March and 27-36 mm from April to October. The average maximum temperature is 31°C and the minimum is 21°C. The former varies between a range of 19-42°C and the latter between 7.5° and 30°C. The mean daily range of temperature varies between 25°C and 27°C from November to

February, it is 16°C to 18°C during April, May and October and 8°-10°C from June to September. The wind speed is 6-8 knots from April to September and 2.4 to 4.7 knots from October to March. The mean number of rainy days is 10 with a maximum of 90 to 100 mm in July followed by 55 mm in September and 25 mm in December while

Table 4. Calculated salt concentration in the brines of salt works

| Sl. No. | Percentage of Salt | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---------|--------------------|--------|---------|---------|---------|---------|---------|--------|---------|--------|---------|---------|
| 1. | Sodium Chloride | 3.0502 | 14.2341 | 10.9297 | 3.0502 | 9.6588 | 11.6923 | 4.0669 | 14.9966 | 3.3043 | 7.7312 | 18.3010 |
| 2. | Potassium Chloride | 0.1907 | 0.5721 | 3.2417 | 0.1907 | 0.3814 | 1.3348 | 0.1907 | 1.5255 | 0.1907 | 0.3814 | 0.1907 |
| 3. | Magnesium Chloride | 0.4307 | 1.7900 | 6.0238 | 0.5091 | 1.2973 | 4.9567 | 0.5236 | 6.0869 | 0.6113 | 1.2734 | 6.8325 |
| 4. | Magnesium Sulphate | 0.2980 | 1.2284 | 2.5580 | 0.259 | 1.0090 | 4.0880 | 0.4213 | 2.4785 | 0.3104 | 0.7377 | 4.3652 |
| 5. | Calcium Chloride | — | — | — | — | — | — | — | — | — | — | — |
| 6. | Calcium Sulphate | 0.1359 | 0.5445 | 0.2042 | 0.1359 | 0.4083 | 0.2721 | 0.1359 | 0.2042 | 0.1359 | 0.2721 | 0.1359 |
| | T.D.S. | 4.1055 | 18.3691 | 22.9574 | 4.14553 | 12.7548 | 22.3439 | 5.3384 | 25.2917 | 4.5526 | 10.0358 | 29.8253 |

April, May and October are usually dry months.

The extent of natural solar evaporation depends on the meteorological conditions. It may be seen from the above that the atmospheric temperature ranges between 20° and 40°C from winter to summer. The relative humidity is minimum during the colder part of the night. The more the minimum humidity the better is the evaporation rate. The equilibrium relative humidity in which salt crystallizes out is 74 % for a brine density of 1.200 and 68 % for a density of 1.257 [3]. The minimum relative humidity under which salt can crystallize out is approximately 70 % and this condition is attained from late April to middle of November and, therefore, these are the ideal months for solar salt production in Pakistan. From November to March dry desert winds dominate over the coastline and the humidity falls. During this period there is evaporation of the brine but also a selective precipitation of magnesium sulphate.

Sea water as it enters the salt works evaporates at different rates in winter and summer. Evaporation is slowed down at different stages because of the variation in the relative proportion of ionic species and formation or separation of various double salts or phases. Advantage can be taken of these variations and the different phases can be isolated during the crystallization pan operations.

It would be noted from the analysis of brines from different salt works and the typical variation in the properties of coastal waters [4], listed in Table 3 and 5, respectively, that the salinity of sea water on Karachi seashore is slightly higher than the average. In the shallow Manora Channel the high salinity leads to increase in the individual ions concentration above that of normal sea water.

In the initial stages of its evaporation sea water loses two of the minor components, *viz.* iron and calcium carbonate [5]. Such deposits have not been found in the salt works under review. Gypsum crystallizes at a density of 13 to 26°Be [5], but its crystallization is not complete

and it keeps precipitating along with sodium chloride. Calcium sulphate is deposited in the salt works in the form of marine gypsum crystals of 1.5 to 2.5 cm length and there is an abundance of such deposition in the inlet ponds. This is the first critical stage and these crystals must be harvested but since they do not have any commercial value, they are left in the pond, thus allowing passage of calcium ions into subsequent operations. This is perhaps the main reason for the presence of higher quantities of calcium ions as is noted from the analyses in Tables 2, 3 and 4.

On attaining a concentration of about 11°Be, the brine is circulated through evaporation/condensation ponds and finally allowed to enter into the crystallization pans for obtaining crystalline sodium chloride. Salt is saturated at 25.4°Be and about 78 % of it crystallizes out at a density of 29°Be.

Various double salts crystallize beyond 29°Be when the mother liquor called Bittern is left to concentrate by the combined effect of sun, breeze and cooling at night and some metastable phases of magnesium salts particularly magnesium chloride can be deposited. This density marks the second critical stage [6] and thereafter the liquor should be discarded, otherwise, magnesium chloride impurities would contaminate the salt and make it deliquescent. It may be observed that not only are the magnesium impurities allowed to pass on into the crystallizing salts, as observed from Tables 2, 3 and 4, but fresh and/or semi-concentrated liquor is pumped into the crystallizing pans as would be shown from the following section:

Degradation of the quality of salt. Analysis of sea salt samples listed in Table 2 shows that the sodium chloride content is invariably lower than 98 % as desired by the Pakistan Standards Specifications and Pure Food Laws, 1965 for edible common salt, or Namak and also for industries. The product as available in the market is, therefore, not readily acceptable.

Table 5. Typical variations in the properties of coastal waters

| Characteristic/ constituents | Standard sea water | Point Loma San Diego | Brazosport | Rantam river New Jersey | Karachi harbour (average) |
|---------------------------------------|-----------------------|-------------------------|------------|-----------------------------|------------------------------|
| pH | 8.2 | 8.1 | 8.0 | 7.0 | 7.6 |
| Total dissolved solids (TDS) (ppm) | 35,000 | 33,400 | 36,250 | 24,000 | 37,000 |
| Sulphate | 2,712 | 2,610 | 2,900 | 1,960 | 2,700 |
| Chloride (ppm) | 19,350 | 18,920 | 20,750 | 12,400 | 20,500 |
| Bicarbonate (ppm) | 142 | 104 | 95 | 84 | 200 |
| Calcium (ppm) | 413 | 398 | 430 | — | 480 |
| Magnesium (ppm) | 1,294 | 1,280 | 1,400 | 4,000 as Ca CO ₃ | 1,450 |
| Sodium (ppm) | 10,760 | — | 10,700 | — | 11,500 |
| Potassium (ppm) | 387 | — | 445 | — | 400 |

Table 6. Density and chemical composition of brines

| | 1.020 | 1.027 | 1.030 | 1.037 | 1.069 | 1.095 | 1.139 | 1.169 | 1.202 | 1.241 | 1.276 |
|--------------------------------------|---------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|
| Density | | | | | | | | | | | |
| Sodium chloride NaCl | 3.0502 | 3.0502 | 3.3043 | 4.0669 | 7.3712 | 9.6588 | 14.234 | 11.692 | 14.996 | 18.301 | 10.9297 |
| Magnesium chloride MgCl ₂ | 0.5091 | 0.4307 | 0.6113 | 0.5236 | 1.2734 | 0.2973 | 1.79 | 4.956 | 6.086 | 6.832 | 6.0238 |
| Magnesium sulphate MgSO ₄ | 0.2594 | 0.2980 | 0.3104 | 0.4231 | 0.7377 | 1.009 | 1.2284 | 4.088 | 2.4785 | 4.365 | 2.558 |
| Potassium chloride KCl | 0.1907 | 0.1907 | 0.1907 | 0.1907 | 0.3814 | 0.3814 | 0.5721 | 1.3348 | 1.5225 | 1.907 | 3.2417 |
| Calcium sulphate CaSO ₄ | 0.13559 | 0.1359 | 0.1359 | 0.1359 | 0.2721 | 0.4683 | 0.5445 | 0.2721 | 0.2042 | 0.1359 | 0.2042 |

Insoluble impurities, such as, clay, grit, etc., are usually the result of careless scrapping of salt from the crystallization pond. Dust particles are contributed by the wind blowing over the salt heaps as well as the ponds. Calcium sulphate, magnesium sulphate and magnesium chloride are the common impurities whose total percentage ranges from 3.42 to 9.07 %. As stated earlier, the presence of high quantities of calcium sulphate suggests that there is a lack of quality control at the initial stage of concentration because calcium ions should usually get separated out in the inlet ponds.

Magnesium impurities are a result of admixture with bittern since only in magnesium rich environment would salt carry magnesium ions. The inferences (i) that crystallizers are being charged with brine at improper time when it has passed the point of saturation of sodium chloride and (ii) that there is also considerable delay in the replenishment of crystallizers with saturated brine and a deliberate mixing of 31° to 33° Be density bittern with brine are borne out by biological indicators carried over into the salt works located in the Manora Channel where sewage and industrial effluents from the vicinity are discharged by the Lyari [8]. By chemical and biological standards the water

flowing through this River is strong sewage. Although it may appear from Fig.1 that the river water is dwarfed into the tidal flats and there might be sufficient dilution of the polluted water, a detailed study of the quality of Manora Channel input indicates that the same is heavily polluted [7, 8].

A number of differences can be noted from the analytical data between the sea water brine and that received as input for the salt works. It may, for example, be seen that water from the coastal pump has a pH value between 7.0 and 8.0 (Table 3) and the pH of Lyari water is 6.9 [4]. Furthermore, the pH of concentrated brine is quite high and is of the order of 9.0 or over (Table 3) suggesting that concentration of the brine in salt pans is not being effected in the manner described above and impurities are contributing to alkalinity.

It may be seen from Table 3 that some samples fail the putrescibility test within a few hours. This may be surprising because the brine is usually stored for several hours for achieving the concentration from a density of 1.030 to 1.069 and the aeration by the breeze should deal effectively with putrefying matter. Permanganate No. which to a certain degree is a measure of the amount

of oxygen consumed to react with organic putrefying matter, is also quite high, particularly for samples No.3, 6, 8, 9, 10 and 11. The permanganate No. for the lower density samples like 1, 4 and 7 is quite high compared with Lyari water which is 4.0. The high permanganate consumption value should therefore be due to defective methodology of mixing raw sea water, already loaded with organic matter, with the evaporated brine to obtain rapid evaporation.

A comparison of the calculated salt content as presented in Table 4 with the reported data [9] presented in Table 6, indicates that the composition of brine at different concentrations is in close agreement. Anomalies are noted for sample No.7 for which the concentration of NaCl is considerably lower than expected. This is again indicative of throwing away the bittern, it is diluted with brine of low density. This results in the rapid crystallization of salt but the magnesium content of such diluted liquor is higher than normal. The observed composition of sample No.6, therefore, does not appear to conform with natural processes of sea water evaporation. Dilution in this case apparently has been effected with coastal water and that explains why the sample ultimately discharges methylene blue, although it passes the putrescibility test within stipulated time.

The total dissolved solids content listed in Table 3 when compared with the calculated figures listed in Table 4 are noted to be much higher in concentrated solutions than in dilute solutions. This is particularly the case for samples No.3, 6, 8 and 11. For these samples the loss on ignition is also high. It is difficult to assign a definite reason for this anomaly because a number of ingredients can contribute towards the high difference, some of these could be the presence of organic matter and bicarbonates. The bicarbonate content is rather high compared with seawater which ranges between 80 and 150 ppm. The bicarbonate content of even the dilute brine is above 600 ppm but that of the four samples mentioned above is higher still. This is possibly due to the contribution from the

sewage rich Lyari water mixing up with the salt works input and also due to the presence of red algae quite commonly found in the ponds.

The above observations suggest that the polluted water from Lyari is not sufficiently diluted to bring down the pollution level. It seems that the untreated sewage and industrial effluents discharged from Lyari accumulate in the channels and creeks and are only partly mixed with sea water even during high tides perhaps because of the location of the high water line at a distance of 10 km. The contaminated coastal water brought by the tides into the salt works, the faulty practice of mixing such water into bittern and lack of quality control at each stage of the process are therefore, some of the most likely causes for deterioration of the salt works in general and the available sea salt in particular.

REFERENCES

1. M.A.A. Beg, Nayeemuddin and S.N. Mahmood, An Overview of the Sea Salt Industry in Pakistan, International Symposium on Salt and Marine Chemicals Research, Bhavnagar, India, (1982) p.1.
2. Meteorological Data, supplied by Regional Meteorological Centre, Airport, Karachi.
3. B.P. Choudhari, Salt Res. & Ind., 5, 5 (1968).
4. M.A.A. Beg, S.N. Mahmood, Sitwat Naeem and A.H.K. Yousufzai, Pakistan J. Sci. Ind. Res., 27, 199 (1984).
5. Donald E. Garret, *Proceedings of International Symposium on Water Desalination*, 1st, (Washington D.C., 1965), p. 176.
6. M.H. Jadhav, Salt Res. & Ind., 4, 5 (1967).
7. M.A.A. Beg, S.N. Mahmood and A.H.K. Yousufzai, Proc. Pak. Acad. Sci., 12, 115 (1975).
8. M.A.A. Beg, N. Basit, F. Siddiqui, I. Mahmood, and M.A. Siddiqui, Pakistan J. Sci. Ind. Res., 27, 206, (1984).
9. G.C. Jain, J.M. Patel, R.M. Bhatt and R.B. Bhatt, Salt Res. & Ind., 4, 49 (1967).