

Sea Pollution and Solar Salt

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ABSTRACT

The purpose of this study was to determine the effects of some marine pollutants on the solar salt produced for nutritional use. The conclusion is that inorganic contaminants behave in two different ways, if they crystallize before or together with salt and if they crystallize after. The study was performed first on samples coming from the ponds, in order to verify the behavior of natural contaminants. Adequate analytical techniques were used. In particular, trace metals were determined directly in the brines and in the salt solution without any preconcentration by a flameless atomic absorption method. Moreover, in order to investigate the behavior of the same contaminants under heavy pollution conditions, natural crystallization conditions were reproduced in a laboratory and a magnified artificial pollution was simulated for both the types of contaminating agents. It was verified that, under such conditions, salt of different purity level is obtained according to the type of polluting agent. Ways to obtain salt suitable for nutritional use, even from polluted brines, were tested.

INTRODUCTION

Sea pollution is causing a great concern and trouble all over the world. The aim of studies and investigations on this subject is generally to verify the harmful influence on sea-life conditions and, subsequently, to consider any possible effects on human health. The pollution of solar salt, directly extracted from seawater brine for nutritional uses, is a question which has not been so far faced.

This omission may be justified because crystallization itself is believed to be a purifying process and also because there are several analytical problems in determining trace pollutants in a high-salt matrix.

The purpose of this investigation was to determine the behavior of some inorganic components of seawater, during the crystallization of solar salt, and their influence on the food quality of the produced salt. The analytical troubles were overcome by applying refined techniques. The pollutant agents were determined directly in the brines and in the salt solutions without any concentration or separation treatment that might cause more remarkable errors in the analyses.

METHODS AND DETERMINATIONS

In particular, chelometric methods, spectrophotometric methods in visible region, flame and flameless atomic absorption spectrophotometric methods were applied. There are so many components in the seawater that several equilibria coexist in solution, one influencing the other. Table I shows the concentration of some components of the seawater; sodium and chloride are not included. They are described as major or minor components according to their own abundance. Some reported data were taken from references and they refer to the average concentrations of the open oceans; the others resulted from the analyses carried out on the seawater at the intake pipes of three Italian salt-works. Moreover, the following concentration ranges may be considered. In the Mediterranean Sea, Tatsumoto and Patterson (1963) found 0.00002 -- 0.0002 mg/l of lead and Fonselius (1970) found 0.001 -- 0.026 mg/l of zinc. In the Gulf of Taranto Bernhard et al. (1975) found 0.0058 + 0.024 mg/l of zinc.

Owing to the complexity of the physiochemical equilibria involved, any merely theoretical consideration about

TABLE 1
Concentration of Some Major and Minor Components of Seawater

	Major Components			Minor Components			
	Mg	Ca	K	SO ₄	B	Zn	Pb
Sverdrup, 1954	1,272	400	380	2,649	4.6	0.005	0.004
Goldberg, 1963	1,350	400	380	2,652	4.6	0.01	0.00003
Burton, 1977	1,294	412	399	2,712	4.5	0.002	0.00003
Adriatic Sea, 1975 (Margherita di Savoia)	1,500	400	400	3,100	5.0	0.001	0.001
Mediterranean Sea, 1977 (Cagliari)	1,500	400	380	3,610	4.5	0.004	0.006
Mediterranean Sea, 1977 (S. Antioco)	1,540	360	380	3,090	5.0	0.001	0.002

Concentrations are reported as ppm.

TABLE 2
Concentration of Some Components of Seawater Brine During Solar Evaporation in the Ponds, July 3rd

Sample	Density Bé at 25°C	Mg	Ca	K	SO ₄	B	Zn	Pb
1 Seawater	3.9	1,500	400	400	3,100	5	0.001	0.001
2 Concentrating pond	5.0	2,000	600	500	3,700	15	0.001	0.005
3 Concentrating pond	10.5	4,500	1,200	800	8,700	25	0.002	0.003
4 "Lime" pond	19.5	9,400	800	1,800	14,600	28	0.004	0.002
5 "Lime" pond	20.3	10,600	600	2,500	15,900	50	0.004	0.002
6 Brine to crystallizing ponds	25.6	15,600	400	4,400	16,600	55	0.004	0.004
7 Crystallizing pond	27.7	30,400	400	6,900	39,000	90	0.006	0.001
8 Crystallizing pond	28.4	34,000	400	7,700	38,000	115	0.005	0.001

Concentrations are reported as ppm.

solar salt crystallization would be unreliable if not supported by real data determined in the ponds. Our investigation started by determining the concentration of some components of the seawater brine in the ponds, during solar evaporation. At the saltworks of Margherita di Savoia, eight peculiar points were chosen. The relevant brine samples were taken in the midst of the production season (on July 3rd) and towards the end of it (on July 31st).

Major components. Figure 1 shows the changes in the seawater brine density of the ponds during solar evaporation. Sample 1 is the seawater at the intake pipe; samples 2 and 3 are from the concentrating ponds; samples 4 and 5 are from the intermediate ponds (the so-called "Lime-ponds"); sample 6 is the brine transferred to the crystallizers, samples 7 and 8 are the brines from two of the crystallizing ponds. It may be noted that at the end of the season highly concentrated brines are no more available. The density of sample 6 decreases to 22.6 Bé. Instead, the density values are obviously the highest in the crystallizers.

Table 2 shows the concentration of some components of the seawater brine in the ponds on July 3rd. Among the major components it was found that the concentration of magnesium, potassium and sulphates increased together with density; while the concentration of calcium was maxi-

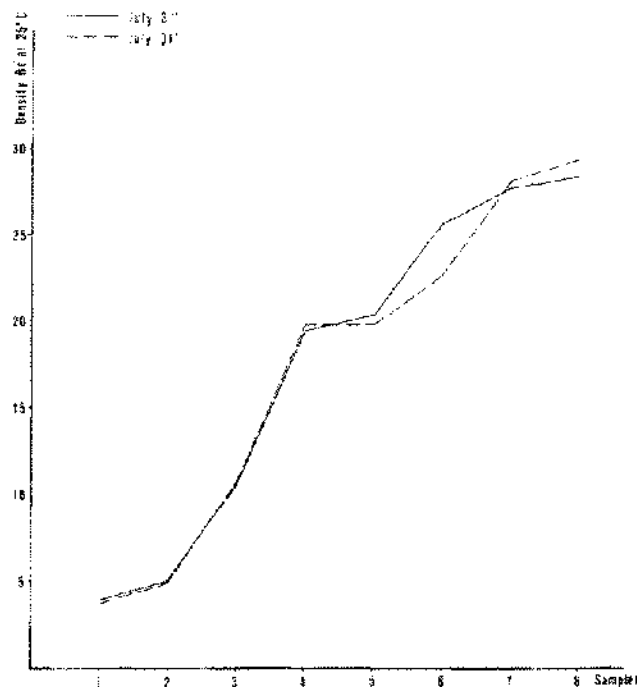


Figure 1. Density of the seawater brine during solar evaporation (Adriatic Sea, Margherita di Savoia).

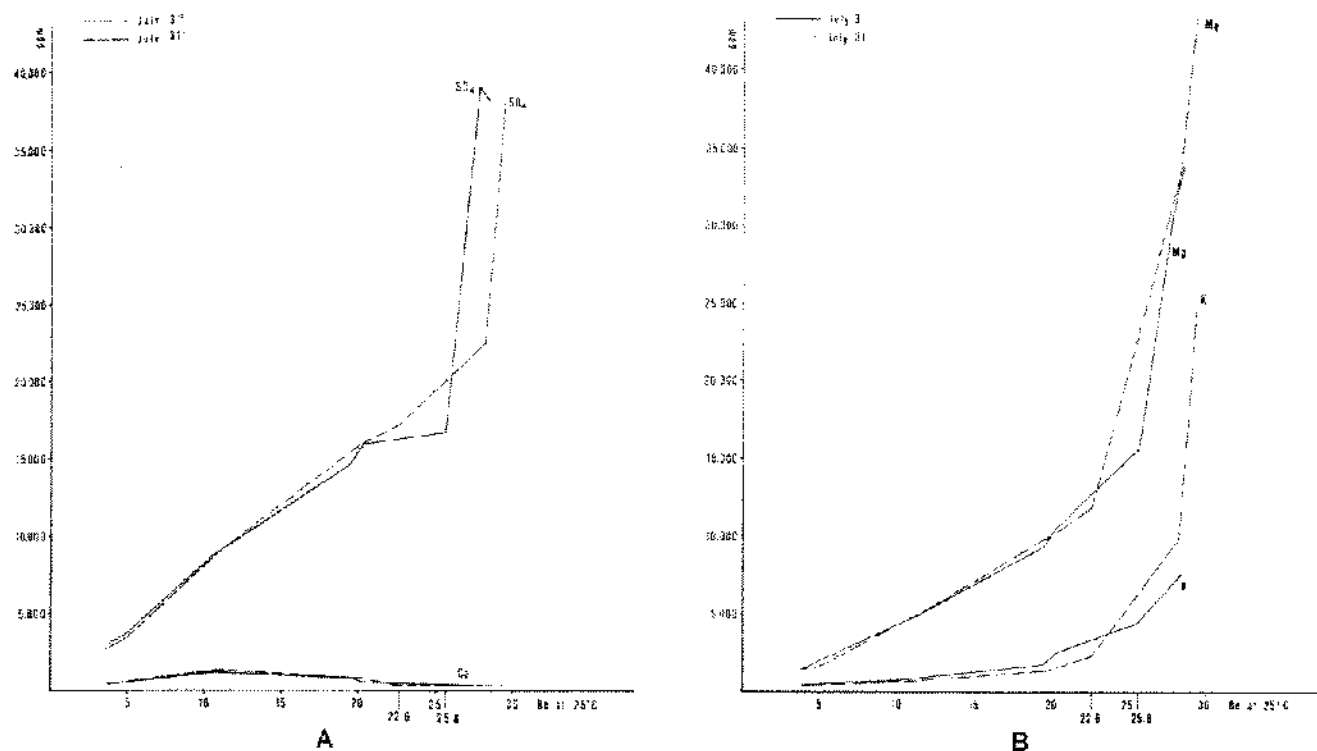


Figure 2. Concentration of the major components in the seawater brine at the various solar pond densities. a) Concentration of calcium and sulphates in the seawater. b) Concentration of potassium and magnesium in the seawater.

TABLE 3

Concentration of Some Components of Seawater Brine During Solar Evaporation in the Ponds, July 31st

Sample	Density Bé at 25°C	Mg	Ca	K	SO ₄	B	Zn	Pb
1 Seawater	3.7	1,400	400	400	2,700	5	0.002	0.001
2 Concentrating pond	4.9	1,600	500	600	3,400	10	0.004	0.002
3 Concentrating pond	10.7	4,600	1,300	700	8,800	20	0.004	0.001
4 "Lime" pond	19.8	10,600	800	1,600	16,300	38	0.020	0.004
5 "Lime" pond	19.8	9,700	800	1,200	14,900	35	0.010	0.002
6 Brine to crystallizing ponds	22.6	11,900	400	2,300	17,100	40	0.005	0.002
7 Crystallizing pond	28.1	32,800	400	9,800	22,400	110	0.004	0.002
8 Crystallizing pond	29.3	43,300	400	25,200	38,000	160	0.005	0.001

Concentrations are reported as ppm.

imum in sample 3, it decreased in samples 4 and 5 (relating to the ponds where calcium sulphate, "lime", crystallizes) and then remained steady.

Minor components. As regards the minor components, the concentration of boron continuously increased together with density, the concentrations of zinc and lead showed a fluctuating behavior. Table 3 reports the concentration of the same components in the brine samples taken in the same points on July 31st. Figure 2 more clearly shows what happens to the major components concentration in the ponds during solar evaporation. It was found almost the same behavior for all the components on both the sampling dates.

However, on July 31st in the last samples the magnesium and potassium concentrations reached higher values (in fact, magnesium and potassium salts start crystallizing after sodium chloride at the highest density values). Sulphates showed concentration figures lower or steady (which may be related to the depositing of sulphates).

Figure 3 shows the change of the concentration of boron in the seawater brine at the various densities of the ponds. Also in this case it was verified that the concentration continuously increased with density, attaining the highest values in the crystallizers on July 31st; in fact, borates crystallize after sodium chloride.

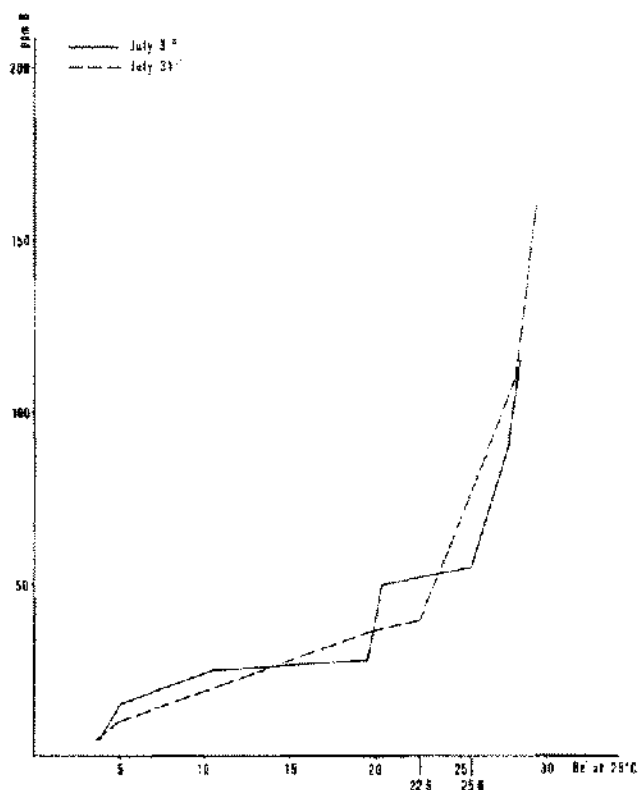


Figure 3. Concentration of boron in the seawater brine at the various solar pond densities.

Figure 4 shows the change of the zinc concentration in the seawater brine at the various densities of the ponds. Samples taken on July 3rd exhibited an increasing concentration up to the crystallizing ponds. On the contrary, samples taken on July 31st showed higher concentration values up to the brine transferred to the crystallizers, with a top in "lime" ponds of density 19.8 Bé, then the various samples from the crystallizers exhibited lower or steady concentration figures. This behavior suggests that, for densities lower than 20 Bé, zinc concentration may increase until attaining the solubility limits of the carbonates and hydroxides and that, in the crystallizing ponds, zinc salts (chlorides or sulphates) start to crystallize as well.

Figure 5 shows the change of the lead concentration in the seawater brine at the various densities in the ponds. As for the samples taken on July 3rd, it may be noted a 5 $\mu\text{g/l}$ top concentration value in the brine from the first concentrating pond, a 4 $\mu\text{g/l}$ top concentration value in the brine of sample 6 and a sharp concentration decrease in the brines of the crystallizers.

As for the samples taken on July 31st, the behavior of the lead concentration was almost the same, but figures are generally lower. In the case of the brines at lower density, lead carbonate and hydroxide depositing may be expected to limit lead solubility, as for the brines from the crystallizers,

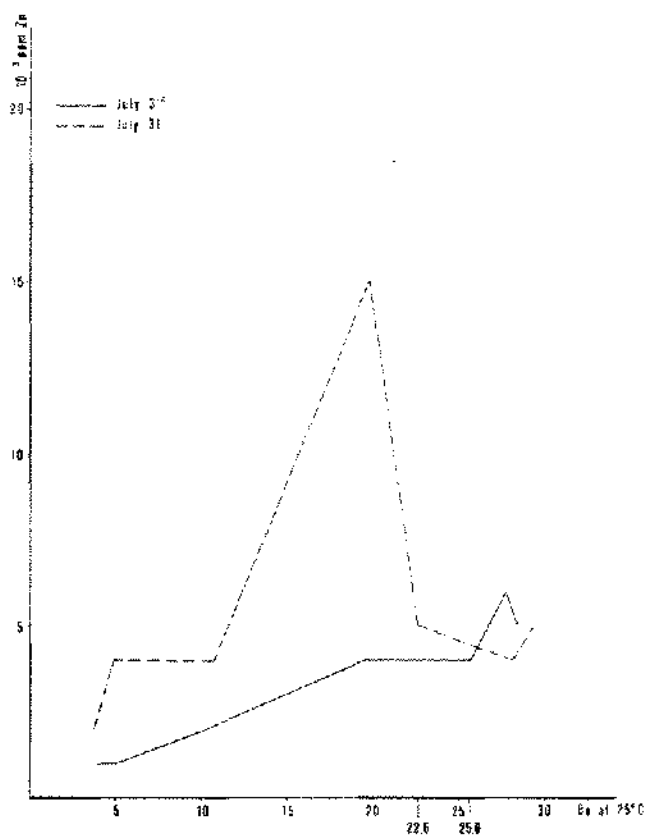


Figure 4. Concentration of zinc in the seawater brine at the various solar pond densities.

lead salts (chlorides or sulphates) may be expected to crystallize jointly with salt.

Natural impurities. Briefly, solar salt contains, as natural impurities, calcium salts ending their own crystallization with that of sodium chloride; lead and zinc salts that crystallize all together with salt; magnesium salts, potassium salts, sulphates and borates that remain out to wet the crystals of the produced salt as components of the mother liquor.

Table 4 shows the content of some natural impurities determined in solar salt from three Italian saltworks for two consecutive years. The 1974 and 1976 data refer to samples taken from the stockpiles and aged for about 1 year. These samples exhibited less humidity and lower contents of magnesium, potassium, sulphates and boron. In fact, during the storage period the stockpile drained and, to some extent, it might be also washed by the rainwater action.

The 1975 and 1977 data refer to samples directly taken from the crystallizing ponds, with the only exception of the sample from the S. Antioco saltworks. This sample was taken from the pile at the beginning of November and thus it showed, after a few months of aging, some dripping effects.

The calcium, zinc and lead contents prove that the storage cannot have any purifying effect on these contaminants. At this point, it appeared interesting to investigate the be-

TABLE 4
Concentration of Some Natural Impurities in Italian Solar Salt

	Year	Loss on Drying %	Mg	Ca	K	SO ₄	B	Zn	Pb
Margherita di Savoia	1974	3.5	1,300	1,900	500	4,860	3	0.55	0.10
	1975	8.4	7,400	1,400	1,800	9,200	25	0.65	0.07
Cagliari	1976	3.6	500	1,600	130	4,200	4	0.12	0.05
	1977	9.7	8,200	2,000	2,550	13,710	21	0.17	0.16
S. Antioco	1976	1.8	1,300	790	170	3,480	5	0.14	0.13
	1977	3.8	3,500	1,700	1,050	8,500	13	0.15	0.05

Concentrations are reported as ppm on dry basis.

havior of some natural impurities, during salt crystallization, under heavy polluting conditions.

Laboratory work. The conditions of natural crystallization were reproduced in a laboratory. Four types of seawater brine at 25.6 Bé were placed in large polypropylene containers and left there to evaporate. The first brine was the seawater brine as it came from the saltworks. It produced the reference salt. The 2nd and 3rd brines were the same seawater brine with some lead solution added to attain, respectively, a 10-fold and a 100-fold Pb concentration. The 4th brine was the first brine with a 100-fold Pb concentration and a 10-fold B concentration.

During the evaporation, the external temperature was maintained at about 35°C by heating for 4 hours a day and it never decreased below 20°C. Crystallization was stopped when the density of the bitterns was about 34.5 + 35 Bé. The crystallized salt was harvested by non-metal spatulas and piled on some little heaps. Samples for analyses were taken after 20–25 days of draining. Table 5 shows the contaminants content of the salts crystallized from the polluted brines and the final densities of the bitterns too.

As for lead, sample 2 showed a concentration about ten times higher than that of sample 1. Samples 3 and 4 showed concentrations only 20 times higher than that of the reference sample. That should confirm what was already verified in the ponds; that the Pb solubility in the seawater brines is limited. Under the crystallizing conditions of brine 4, the maximum concentration of soluble lead may be expected to be 0.1 ppm.

As for the boron, sample 4 exhibited a concentration about 8 times higher than that of the reference sample, which may be related to the lower density of the bittern. The bittern density figures evidenced that it was practically impossible to stop the crystallization at the same time for all the samples.

In order to compare the chemical quality of the polluted salts with the same mother liquor wetting the crystals, a purifying process was accomplished by several consecutive washings with a NaCl (analytical grade) saturated solution. After the washings, the salts were left to drain on vacuum filters until they attained a loss on drying of 1.8% about and

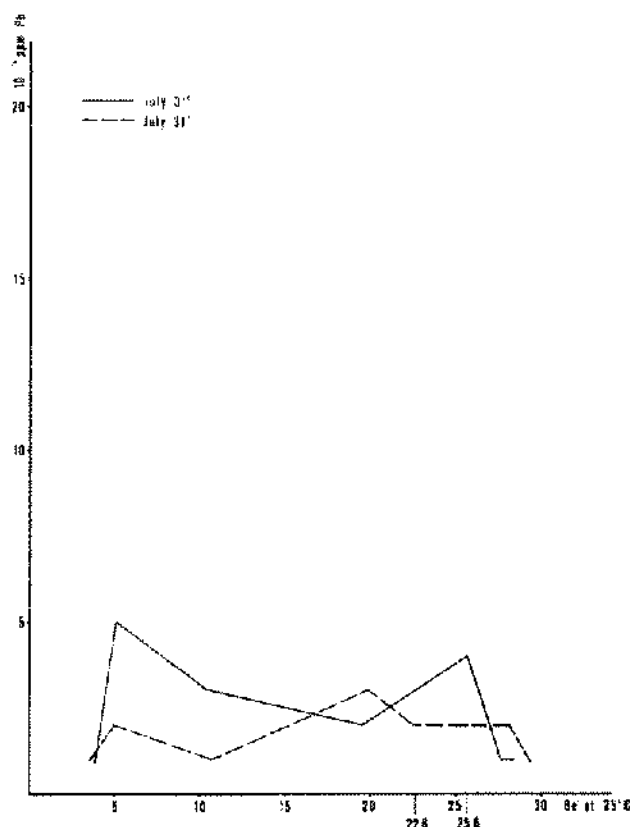


Figure 5. Concentration of lead in the seawater brine at the various solar pond densities.

at last they were dried in an oven. The results of the analyses of samples 1, 2 and 4, after the washing treatment, are listed in the same Table 5.

The following is worth noting. There is a decrease in calcium content, probably because most calcium sulphate crystals dissolved, being external to those of sodium chloride. There is a large decrease in Mg and B concentrations down to the values that may be expected as closely relating to the quality of the occluded mother liquor. Lead content did not change. As for the zinc, it is to be noted that the applied analytical method (flameless atomic absorption spectrometry) exhibited a large coefficient of variation and,

TABLE 5
Contaminants Content of the Polluted Salts Before and After Washing

		Mg	Ca	B	Zn	Pb	Loss on Drying %	Bittern Density Bé at 25°C
1. Reference salt.	b.w.	7,103	627	12.5	0.25	0.05	4.2	34.5
	a.w.	250	67	1.0	0.25	0.05		
2. Salt from brine with 10-fold concentrated Pb.	b.w.	9,778	628	14.6	0.20	0.45	4.3	34.6
	a.w.	280	67	1.0	0.25	0.45		
3. Salt from brine with 100-fold concentrated Pb.	b.w.	10,205	631	16.5	0.25	1.00	4.5	34.8
4. Salt from brine with 100-fold concentrated Pb. 10-fold concentrated B	b.w.	6,950	631	105.0	0.20	1.00	4.6	34.4
	a.w.	210	67	8.0	0.35	1.00		

Concentrations are reported as ppm on dry basis.

TABLE 6
Contaminants Content of Polluted Salt After Laboratory Purification Treatments

		Mg	Ca	B	Zn	Pb
Salt 4	b.w.	6,950	631	105.0	0.20	1.00
	a.w.	210	67	8.0	0.35	1.00
Salt 4 recrystallized	1st fraction	1,825	301	80.0	0.20	1.65
	2nd fraction	2,010	301	120.0	0.20	0.13

Concentrations are reported as ppm on dry basis.

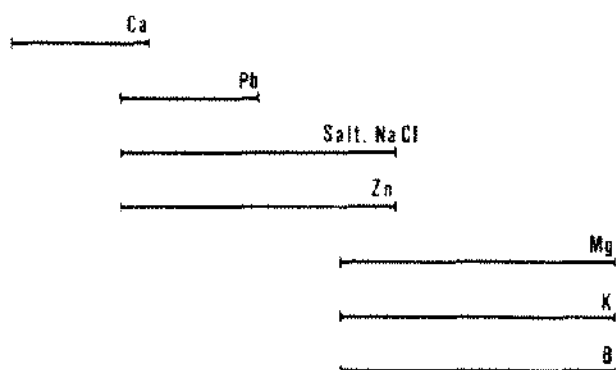


Figure 6. Qualitative sequence of crystallization times.

moreover, the NaCl, used for the washing solutions, contained about 0.5 ppm of zinc.

Next our investigation was aimed at verifying, if possible, the production of a salt free of such contaminants as lead and zinc, which crystallize at the same time. To this purpose, sample 4 was dissolved with distilled and deionized water and then two fractions were recrystallized. The former was about 50% of the initial amount of dissolved salt, the latter was 45%; the brine was not totally evaporated. Table 6 shows the contaminants content in both the recrystallized fractions and, for a better comparison, salt 4 before and after washing.

It is worth noting that the calcium content of both fractions was steady and lower than that of the original salt (in fact, salt 4 solution was not readily saturated with this component). Magnesium and boron contents were generally lower than those of salt 4, though increasing for the 2nd fraction (the salt of this fraction was obviously wet by a bittern more enriched with these components). Most lead crystallized with the first fraction. The zinc content was steady. Figure 6 shows the qualitative sequence of the salt crystallization times and that of some contaminants, as it resulted from this investigation.

RESULTS AND CONCLUSIONS

Considering that solar salt is used for nutritional purposes, a seawater brine polluted by lead might result in a maximum Pb content in the salt of 1 ppm, a figure which could be lowered by discarding the first fraction of crystallized salt. In the case of zinc pollution, the only limiting factor appears to be the poor solubility of such compounds as carbonates and hydroxides; however, further studies will be carried out on this subject. In the case of a seawater brine polluted by boron, salt may be recrystallized, lowering the boron amount occluded with the mother liquor in the crystals, or it may be enough to wash the harvested salt on the stockpiles.

The conclusion of this study is that inorganic contaminants differently influence the solar salt purity level according to the sequence of the crystallization times. At present, sea pollution is not at all a source of concern to the production of food grade solar salt, since the contents of the contaminants are very low and in any case far from reaching dangerous levels to human health.

However, considering the large and particular use of salt, since 1973 the Italian Monopoly has been making periodic checks at each of its saltworks in order to guarantee the food grade quality of the salt produced.

Furthermore, I would like to add that my Company gave the University of Bari the assignment of carrying out a microbiological investigation on the influence of bacteria and viruses. For the pathogenic bacteria the research showed that at present there is no pollution and that even under artificially magnified polluting conditions their lifetime is shorter than the time required for solar salt crystallization in the ponds. This is true also for those bacteria that are the most resistant in a salt medium.

The study is still being pursued on the viruses, but we believe that the final results will have similarly optimistic conclusions.

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