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PREVENTION OF CALCIUM SULPHATE SCALE FORMATION IN EVAPORATION PLANTS BY ION EXCHANGE

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SUMMARY

A process has been developed that enables sulphate in sea-water feed to distillation plants to be replaced by chloride ions by means of weak anion-exchange resins. Calcium sulphate scales are thus prevented from forming on heat-exchange surfaces. Only the blow-down discharged from the evaporation plant is used to regenerate the resin. After a preliminary evaluation on a laboratory basis, pilot-plant tests, run for about 7500 h on a combined multflash–desulphation unit, fully confirmed the feasibility of the process. Based on these results, a 2000 m³/d advanced multflash plant will be erected near Bari with a maximum operating temperature of 150° and a recovery ratio of 20 kg of water per kg of vapour.

INTRODUCTION

Sea-water dealkalization enables distillation plants to be operated at 110–115° with a concentration ratio (n) of about 1.8. This corresponds to metastable conditions for the anhydrous calcium sulphate solubility, and frequent descaling maintenance operations are commonly scheduled in such plants. Fig. 1 shows, as an extreme case, a cross-section of a heat-exchange tube of a multflash evaporator run for about 700 h at 110° and $n = 1.8$; the tube is obstructed by calcium sulphate scale. Higher operating temperatures could theoretically reduce the cost of producing water¹, but it would produce intolerable scales.

In order to overcome this problem, systematic investigations have been carried out by IRSA with the aim of removing the sulphates from sea water by means of anion-exchange resins, using only concentrated sodium chloride solution discharged from the evaporation plants as regenerant. An extensive research programme has been carried out during the last 4 years, which first included basic investigations on the equilibrium and kinetic features of many anion-exchange resins toward the Cl⁻–SO₄²⁻ system. This led to the selection of a particularly suitable resin, which was subsequently characterized by laboratory tests so as to obtain design data for a pilot-scale evaluation of the process. A desulphation unit was then built in order to pre-

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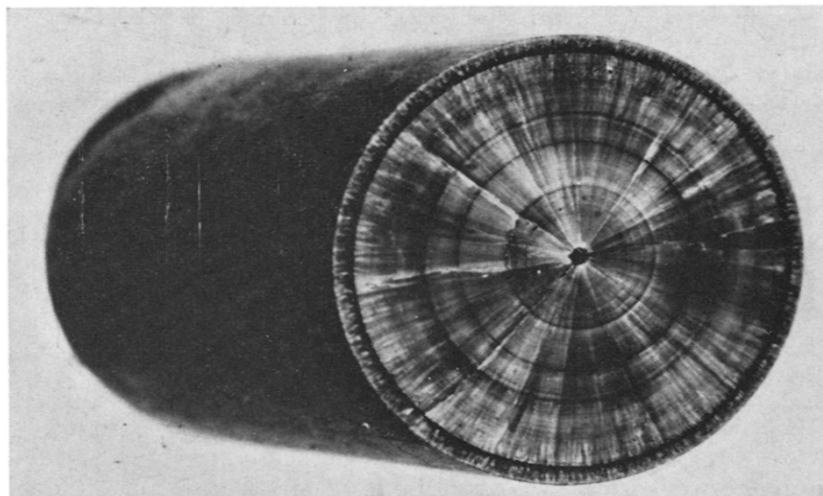


Fig. 1. Cross-section of a heat-exchange tube of a multflash evaporator encrusted by calcium sulphate scales. Operating temperature, 110° ; concentration ratio, $n = 1.8$.

treat the feed of a $100 \text{ m}^3/\text{d}$ multflash pilot plant. About 7500 h of effective service of the pilot unit, under various and severe operating conditions, definitely confirmed the suitability of the process. After this experience, a $2000 \text{ m}^3/\text{d}$ multflash plant with a desulphation unit has now been planned as the first industrial application of a high temperature, high recovery ratio evaporation plant.

This paper summarizes the main results obtained during each stage of the research programme.

BASIC INVESTIGATIONS

First, the thermodynamics and the kinetics of the $\text{Cl}^- - \text{SO}_4^{2-}$ exchange on more than 30 anion-exchange resins have been investigated. Using the column equilibration procedure and the infinite batch technique for the selectivity and the kinetic measurements, respectively, equilibrium isotherms and the exchange rates were determined for each resin, with solution concentration ranging from $6 \cdot 10^{-3} N$ (i.e., $n = 10^{-2}$) to $1.8 N$ ($n = 3$), temperatures between 5 and 45° , and a pH of about 3.5. The resin performances were found to be essentially dependent, among the investigated parameters, on the fixed charge basicity, and the following sequences were obtained^{2,3} (Figs. 2 and 3):

(1) Selectivity sequence: $\text{IV}^{\text{ary}} < \text{III}^{\text{ary}} < \text{II}^{\text{ary}} < \text{I}^{\text{ary}}$ amino-type resins.

(2) Kinetic sequence: $\text{IV}^{\text{ary}} > \text{III}^{\text{ary}} > \text{II}^{\text{ary}} > \text{I}^{\text{ary}}$ amino-type resins.

The following conditions were also found to favour the process, although less significantly: high temperature; low pH; low solution concentration; hydrophilic, porous matrix; 10–12% cross-linking; high exchange capacity.

As a result of these investigations, a high-capacity, 11% cross-linked, acrylic resin with predominantly secondary (and primary) amino functional groups (Kastel A 102, produced by Montecatini Edison Co., Milan, Italy) was selected for further research development. This resin is characterized by the following features:

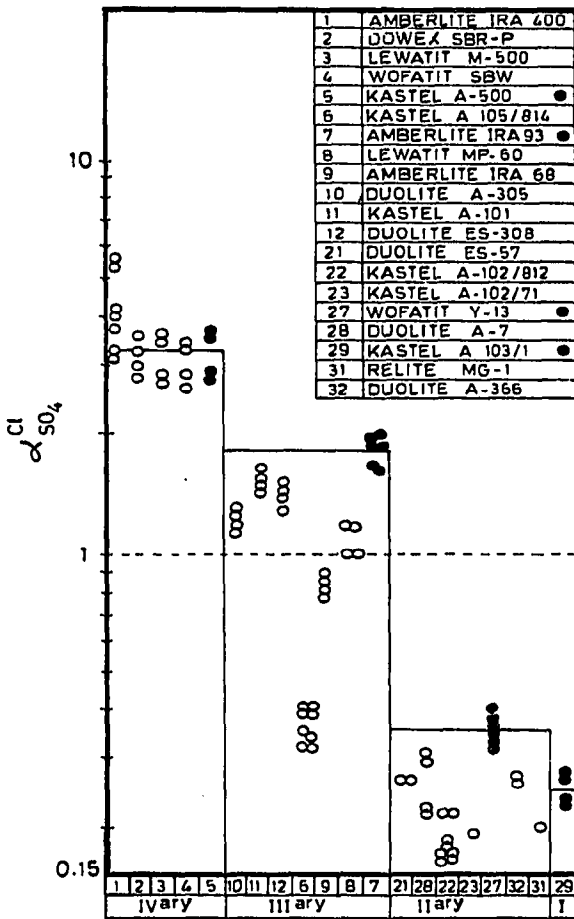


Fig. 2. Cl⁻-SO₄²⁻ separation factors versus predominant functional group of anion-exchange resins. Separation factor, $\alpha < 1$, selectivity toward sulphates. Solution concentration, $C = 0.6 N$; sulphate equivalent fraction in solution, $X = 0.5$; 25°.

- (a) extremely high selectivity toward sulphates at sea-water salinity (about 0.5 equiv. SO₄²⁻/equiv. resin under equilibrium conditions);
- (b) strong decrease in selectivity by increasing the solution concentration (more than a 50% decrease by a two-fold increase in the solution concentration);
- (c) very high exchange rate at solution concentrations equal to or higher than sea water (half-exchange times less than 1 min).

LABORATORY RUNS

More than 250 countercurrent exhaustion-regeneration cycles were run on a 5-1 column filled with Kastel A 102 resin, with sea water (previously acidified at a pH 3.5) fed upwards. Synthetic sodium chloride solutions were used as regenerant. The dependence of resin performance on the main operating parameters (blow-down concentration, exhaustion and regeneration flow-rates) was characterized.

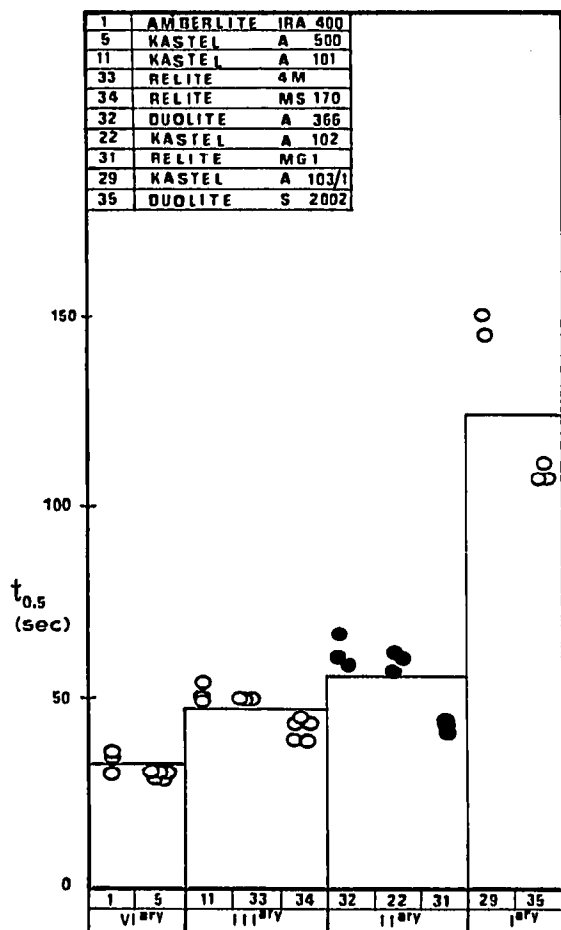


Fig. 3. Cl^- - SO_4^{2-} half-exchange times versus predominant functional group of anion-exchange resins. $C = 1.8 N$; 20-30 mesh; 25°.

Blow-down concentration

As the concentration ratio increases, higher degrees of desulphation may be obtained in the treated water (see Fig. 4). From a practical point of view, higher n values mean less sea water to be treated per unit volume of water produced and less heat to be discharged with the blow-down. On the other hand, corrosion problems and ebullioscopic losses make it difficult to use n values higher than 2.5-3.0 with traditional evaporation plants.

Exhaustion flow-rate

The determination of the breakthrough curves at different solution flow-rates (see Fig. 5) confirmed the very high exchange rates previously observed with this resin in batch experiments. At flow rates higher than 40 bed-volumes per hour, up to 20 bed-volumes of sea water may be treated with a degree of average desulphation $\geq 75\%$, depending on the blow-down concentration.

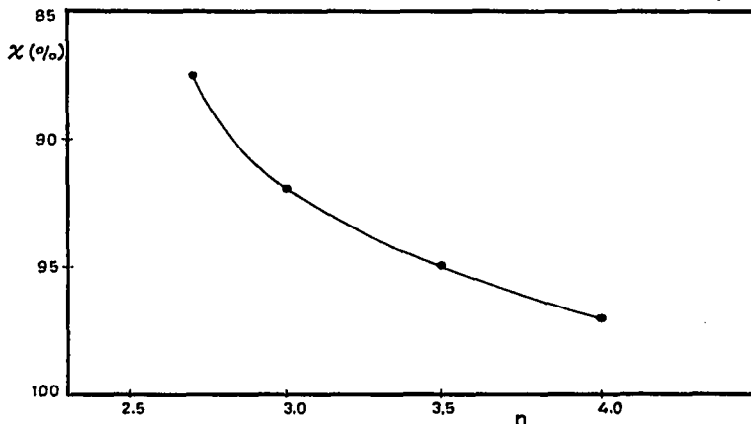


Fig. 4. Average degree of desulphation (χ) versus concentration ratio (n); each point represents the average of 10 cycles. Kastel A 102 resin; cycle volume of treated sea water, $V_{es} = 16$ bed volumes; exhaustion flow-rate, $F_{es} = 40$ bed volumes per hour; volume of blow-down, $V_{rlg} = V_{es}/n$.

Regeneration flow-rate

As the selected resin is still selective toward sulphates at $n = 4$, the regeneration step was thermodynamically unfavourable. Further, simplified plant operations (two columns in parallel, one regenerated while the other was being exhausted, no intermediate operations being necessary on a routine basis) made it necessary to assume equal times for regeneration and exhaustion operations.

The regeneration and exhaustion flow-rates were thus correlated, according to the equation

$$F_{rlg} = F_{es}/n \tag{1}$$

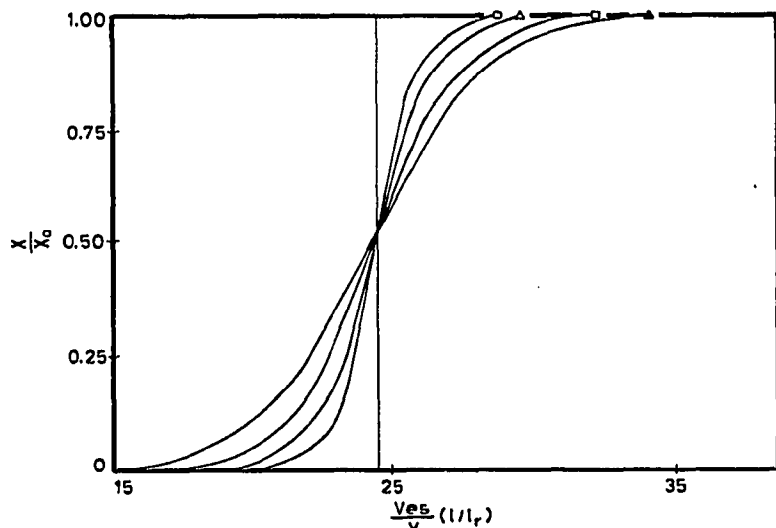


Fig. 5. Sulphate breakthrough curves during the exhaustion step. Kastel A 102 resin; $C = 0.6 N$; $c_{so} = 0.056$ equiv./l; sea-water pH = 3.5; $n = 3$. F_{es} : \circ , 5 bed volumes per hour; \triangle , 10 bed volumes per hour; \square , 20 bed volumes per hour; \blacktriangle , 40 bed volumes per hour.

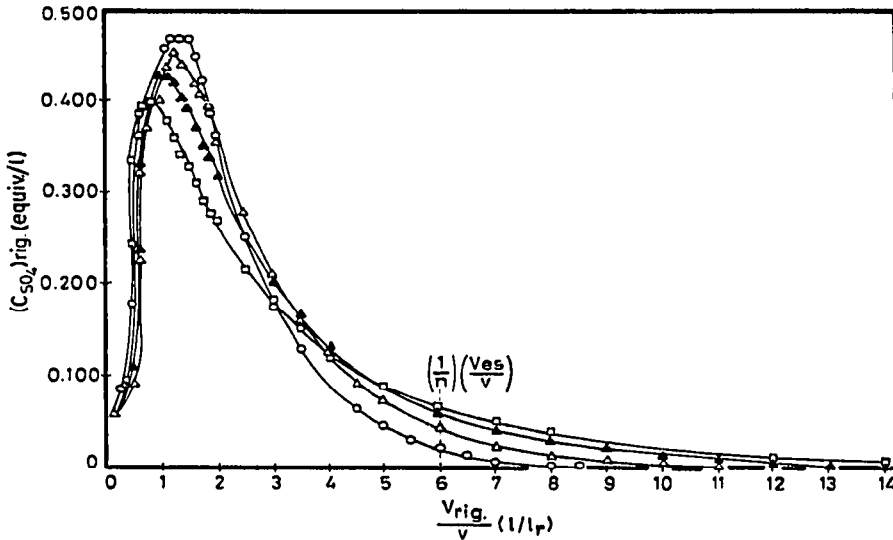


Fig. 6. Sulphate breakthrough curves during the regeneration step. Kastel A 102 resin; $n = 3.5$. F_{rig} : \circ , 0.5 bed volumes per hour; \triangle , 1 bed volume per hour; \blacktriangle , 5 bed volumes per hour; \square , 10 bed volumes per hour.

As indicated by the breakthrough curves obtained during this step (see Fig. 6), the blow-down regenerating capacity was strongly dependent on the liquid–solid contact time.

At each n value, according to eqn. 1 and based on sets of breakthrough curves as in Figs. 5 and 6, a suitable F_{es} value must be chosen that prevents sulphates from accumulating on the resin in each cycle. At the same time, only the last fraction (about 25%) of the (partially) exhausted blow-down was recovered in each run, to be used as first fraction in the subsequent regeneration so as to prevent dilution of the regenerant by the intraparticle bed solution. The laboratory runs demonstrated the suitability of the desulphation process and allowed design data for a larger, pilot unit to be obtained (Table I).

PILOT PLANT TESTS

A four-stage recirculation multflash plant, with an output capacity of about 100 m³/d, still existing at Breda Research Institute facilities in Bari, was served by a desulphating unit consisting of two columns in parallel, each containing about 300 l of Kastel A 102 resin. Fig. 7 shows the operating flow-sheet of the plant. Two series of runs were made, at “low” temperatures (operating temperature between 120 and 130°, $n = 2.5$ – 2.0) and at “high” temperatures (145°, $n = 2.4$), for a total of 7500 h of effective service. The pH of sea water was maintained between 3.5 and 5.0, while after the degasifier a pH of about 7.2 was kept constant. No scales were observed during these runs, even at the highest temperatures.

The first series of runs confirmed the reliability of the desulphation process in conventional evaporation plants, indicating its capacity to re-adsorb occasional breakthroughs that occur as a result of accidental errors. The high-temperature tests

TABLE I

OPERATING CONDITIONS AND RESULTS FOR KASTEL A 102 ANION-EXCHANGE RESIN

Laboratory-scale plant.

Conditions	Concentration ratio, <i>n</i>					
	3.0		3.5		4.0	
Exhaustion flow-rate (l/h)	40.0		40.0		40.0	
Regeneration flow-rate (l/h)	13.3		11.4		10.0	
Sea-water pH	3.5		3.5		3.5	
Cycle volume of treated water (l/h)	16.0	17.5	16.0	17.5	16.0	17.5
Cycle volume of brine (l/h)	5.3	5.8	4.0	5.0	4.0	4.4
Average sulphate removal (%)	92.0	86.5	95.0	90.5	97.0	92.5
Recovered brine fraction	0.25		0.25		0.25	
Resin volume/product water flow-rate (l/h/m ³)*	75.0		70.0		66.6	
Cycle number per year**	3200	3500	3200	3500	3200	3500

* In two columns.

** 8000 h per year.

demonstrated the possibility of preventing, by means of this pre-treatment, the formation of calcium sulphate scales even under very severe conditions, thus allowing for the design of advanced evaporation plants.

Continuous control of the sulphate concentration in the brine, measurements of the fouling coefficient of the condenser tubes and periodic inspections of the heat-exchange surfaces (where sometimes small amounts of iron oxide scales, containing only traces of calcium sulphate, were found) and of the resin beads, fully confirmed the suitability of the desulphation process.

Particular attention was paid to control of the resin life during these tests. After about 7500 cycles (each complete cycle lasting for about 1 h), samples of resin were examined for total exchange capacity, granulometric analysis, etc., while internal

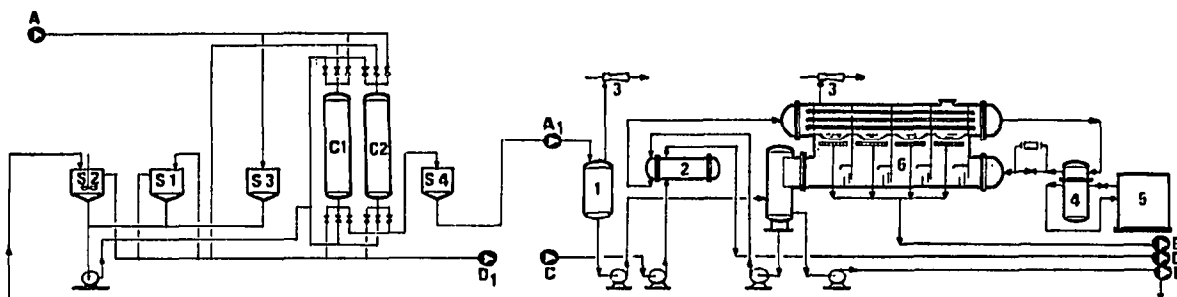


Fig. 7. Operating flow-sheet of the combined desulphation-multiflash pilot unit. A = feed water; A₁ = desulphated water; B = product water; C = cooling water inlet; D = cooling water outlet; E = brine outlet; D₁ = exhausted brine discharge; S1, S2, S3 = regenerant tanks; S4 = desulphated water tank; C₁, C₂ = ion-exchange columns; 1 = degasifier; 2 = brine cooler; 3 = ejectors; 4 = brine heater; 5 = steam generator; 6 = four-stage flash unit.

fouling was checked by X-rays and electronic scanning. All of these controls indicated the excellent features of the resin, as expected according to the very weak chemical and osmotic shocks that occurred during the process. No consumption of resin was detected at the end of the tests.

DEMONSTRATION PLANT

Based on the pilot-plant experiences, an advanced multistage plant with 68 effects, 2000 m³/d capacity is under construction in Bari's industrial area. A maximum operating temperature of 150° and a conversion ratio of 20 kg of water per kilogram of vapour have been adopted, while at n values near 2 the thermodynamic losses due to the elevation of the boiling point would be as in conventional evaporation plants.

Other than for demonstration purposes, the plant will provide data for the design and construction of high-temperature stages.

CONCLUSIONS

Laboratory and pilot-plant experiences have demonstrated the possibility of removing sulphates from sea-water feed to desalting evaporation plants by means of weak anion-exchange resins. These plants can thus be run at temperatures up to 150–160°, at the same concentration ratios as in conventional plants, without the formation of calcium sulphate scales.

A feasibility study on a 10,000 m³/d single-purpose multistage plant demonstrated that with this kind of pre-treatment, the cost of the product water can be de-

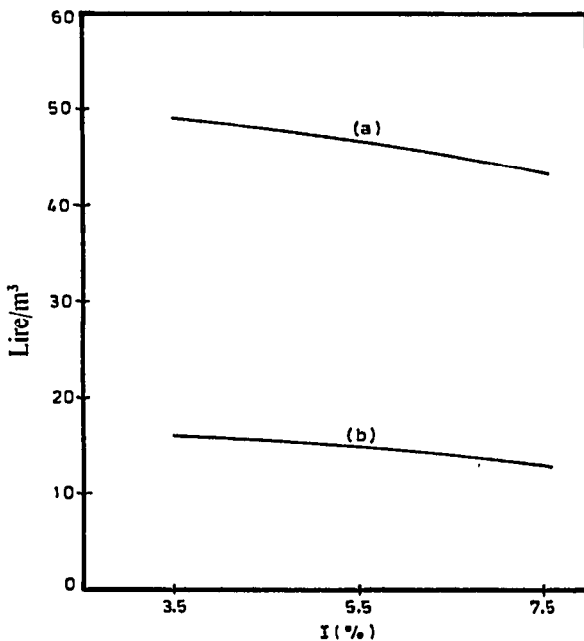


Fig. 8. Savings attainable with the desulphation process as a function of interest rate. Fuel costs: (a) 3500 Lire/10⁹ cal; (b) 1500 Lire/10⁹ cal.

creased considerably⁴. As indicated in Fig. 8, the savings are directly related to the fuel cost. With today's energy shortages, the actual savings are near the upper curve of this diagram, which means about 45 Lire/m³ (US\$0.30 per 1000 gal) of treated water. Even for dual-purpose evaporation plants, the desulphation process allows for appreciable savings owing to the possibility of raising the maximum operating temperature and of maintaining the heat-exchange coefficients at their maximum values.

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