MAGNESIA FROM SEA WATER

The Dolime Process at the Palliser Works, Hartlepool

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Abstract of a Paper read before the Chemical Engineering Group
of the Society of Chemical Industry, London, October 25, 1949

Reprinted from

FLUID HANDLING
33 South Audley Street, London, W.1
January and February, 1950

The photograph shows a general view of the plant from the north of the site, showing a settling tank in the centre foreground. Almost immediately behind can be seen the Hydrotreator, to the left of which are visible parts of the sea water intakes.

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The Dolime Process at the Palliser Works of the British Periclase Co., Ltd

By H. W. THORP, BSc M.I.Chem.E., A.R.I.C.
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Below is an abstract of a paper presented by these authors recently to a meeting of the Chemical Engineering Group of the Society of Chemical Industry. We are indebted to both authors for assistance and to Mr. T. Kirkup, the General Manager of the Palliser Works, and to the Directors of the British Periclase Co., Ltd. for permission to reproduce the photographs.

Extraction of magnesium hydroxide from sea-water was not, the authors claimed, a new process and in a brief historical survey they referred to German patents of some forty years ago.

In this country magnesium oxide and carbonate for insulation and pharmaceutical purposes had been made at Washington, County Durham, by the Pattinson process for many years: similarly refractory pro~ ducts based on dead burned magnesian limestone had been produced at Steetley, near Worksop, for upwards of fifty years.

Precipitated magnesium hydroxide from seawater was of more recent date and the authors confined their paper to the production of dead burned magnesium oxide for use as a steelworks refractory.

In this abstract of a very interesting and well presented paper attention will be focused upon the fluid handling problems involved.

In 1937 the Steetley Company built a pilot plant near Hartlepool on the N.E. coast, followed by a plant to produce 10,000 tons a year of dead burned magnesium oxide. Other demands were made for various purposes during the war and consequential developments took place. Towards the end of the war, however, the demand for magnesium metal (and hence for lightly calcined magnesium hydroxide) fell rapidly to zero. Large quantities of dead burned magnesium oxide, nevertheless, were and still are required by the steel industry so that the Hartlepool works capacity has been increased and further extensions are now in hand.

In their paper the authors describe the process operated by the British Periclase Company at Hartlepool pool which is satisfactory for the materials there available and for operation under British conditions 'of climate and labour.

Apart from fuel, only two raw materials are required, magnesian limestone and seawater.

Sea-Water

The composition and temperature of sea-water varies but little from place to place on the coasts of the British Isles. In siting a works using seawater, however, it is important to avoid parts of the coast where very heavy seas are of frequent occurrence and it is also important to select a place where there is no possibility of dilution by fresh (river) water, and where the tides do not cause re-cycling of spent sea-water. Hartlepool, on the N.E. coast about thirty-five miles south of Newcastle and nine miles north of the Tees mouth, is satisfactory from these points of view as a strong tide sweeps north and south along the coast and thus avoids trouble due to re-cycling, while the Tees is sufficiently far away for its dilution effects to be negligible.

Magnesian Limestone

Since limestone can be used in the sea-water process, it is clear that any magnesian limestone is suitable inasmuch as its magnesium content is added to that of the sea-water. Broadly speaking, the most suitable material is the richest magnesium containing rock which is too poor to be used directly for its magnesium content, since the higher the magnesium content, the less the sea-water required for a given magnesium oxide output. In practice, it is necessary to strike a balance between purity and magnesium content, since calcium carbonate is more widely distributed than magnesium limestone and occurs in a high state of purity more frequently. At Hartlepool there is a considerable bed of magnesian limestone at low level, which, however, is more conveniently quarried where it comes to the surface at Coxhoe, seventeen miles distant. The Coxhoe stone is quarried, crushed, screened and then calcined in “mixed feed" lime kilns with coke as fuel. Since the sole outlet for dead burned magnesium oxide is found in the steel-making industry a high degree of purity in the final product is demanded. An important factor is the purity of the calcined magnesian limestone since the refractories industry ask for a low calcium content and any unchanged calcium carbonate as well as overburned material can-pass through the process and appear in the final product. From Coxhoe the calcined dolomite is carried in sheeted wagons to Hartlepool, and despite all precautions a small carbon dioxide increase is found to occur en route. A mixed feed lime kiln is also in operation at Hartlepool and although the extra cost of transporting raw stone from Coxhoe has to be borne it offers the advantage of good lime which can be graded and crushed on site and taken to the hydration plant by belt conveyor.

Chemistry of the Process

The extraction of magnesia from sea-water depends upon the very small solubility product of magnesium hydroxide whereby it may readily be precipitated from solutions of its salts by bases capable of providing a moderate concentration of hydroxyl ions. Calcium hydroxide has been the base most widely used in commercial operations for this purpose because of its low cost and the abundance in nature of calcareous rocks. When these contain magnesium carbonate a mixture of calcium and magnesium oxides is obtained on calcination and the magnesia product resulting from reaction with sea-water is partly derived from this and partly from the limestone. Basically, therefore, the chemistry of the dolomite and sea-water process is very simple. Dolomite is calcined to give a mixture of calcium and magnesium oxides known as "dolime",

$MgC0_3.CaCO_3$ ----> $MgO + CaO + 2CO_2$

which are added to sea-water when the calcium oxide, after hydration, reacts with the magnesium salts, precipitates magnesium hydroxide and passes into solution

$CaO + H_20$ ---> $Ca\ (OH)_2$,

$Ca\ (OH)_2 + Mg^{2+} \rightarrow Mg\ (OH)_2 + Ca^{2+}$

while the magnesium oxide undergoes some hydration but is otherwise unchanged and is recovered with the precipitate.

As the authors pointed out this is a greatly simplified explanation of the problems involved. Dolomite and fuel are never free from impurities, whilst sea-water contains a great variety of ions. The preparation of a base material having the minimum quantity of - insoluble impurities is of prime importance for the manufacture of a high quality product. To the same end, that of product purity, the prior removal of those substances or ions in sea water which either would be precipitated or would give rise to the precipitation of calcium compounds during the recovery of the magnesia is desirable even though not always practicable. The addition of lime to sea-water to precipitate all (99.9 per cent.) of its magnesium content involves an increase in the hydroxyl ion concentration corresponding to a change in pH value from approximately 8.1 to approximately 11.0 and an increase in the calcium ion concentration from the original 10.23 mg ions per litre to a final 65.3 mg. ions per litre. At equilibrium under these conditions over 99 per cent of the bicarbonate ion and some 20 per cent of the sulphate ion are precipitated as their respective calcium salts, while a substantial proportion of the boron, which in sea water is present partly as undissociated H_3B0_3 and partly as the borate ion $H_2BO_3^-$ becomes associated with the magnesium hydroxide.

On the physical side the main problem in the recovery of magnesia from sea water lies in the difficulty of precipitating the magnesium hydroxide in a form which will settle rapidly and which will yield a sludge easy to de-water The magnitude of the problem is shown by the fact that each ton of magnesia must be separated from some 300 tons of water.

Precipitation of the Magnesium Hydroxide

The reaction between the prepared base (the dolime) and the sea-water is the crux of the process. The objects to be achieved are four-fold:

(1) To proportion the lime and the sea-water correctly.

(2) To ensure complete reaction of the calcium oxide in the lime or dolime.

(3) To precipitate the magnesium hydroxide in a form that will settle rapidly and will yield a sludge easy to de-water

(4) To prevent as far as possible the precipitation of substances other than magnesium hydroxide from the seawater.

The Hartlepool Reaction Systems

At Hartlepool the reaction systems are being operated to give complete precipitation of the magnesium ions; control of high precision being maintained by adjusting the sea-water flow on the basis of frequent chemical tests for hydroxyl alkalinity of the filtrate from the reaction mixture.

The practice of removing the bicarbonate hardness of natural waters by lime in the presence of an active sludge of previously formed calcium carbonate has been well established for some considerable time, but with the equipment formerly available the settling rates of the precipitated solids were generally so low as to render impracticable the application of the process to the quantities of sea-water which must be treated in the commercial recovery of magnesium hydroxide. More recently improved machines in which settling rates, for the precipitated solids, of several feet per hour are attained have become available. At Hartlepool the Dorr Hydrotreator is used.

This machine consists of a round tank having three separate and distinct zones. In the lower portion of the tank is the flocculation zone where the raw water is gently mixed with dolime and previously formed flocs that are automatically returned by gravity from the superposed clarification zone. In this latter zone the flocculated solids are separated from the water which discharges at the surface over a weir into a peripheral launder. Immediately below the flocculation zone at the tank centre is a zone of thickening where excess sludge is continuously concentrated to a minimum water content before discharge.

A variable speed drive rotates the mechanism in the lower portions of the tank through a centre shaft attached to which are perforated distributor arms to give a uniform discharge of the raw water over the tank area. Directly above the distributor arms is the flocculation zone into which the dolime cream is introduced through pipes at one or more points. Vertical paddle blades attached to the rotating distributor arms and intermeshing with stationary blades provide the gentle agitation that promotes rapid diffusion of the dolime and effective mixing of the water with the solids in the sludge blanket. Also attached to the rotating arms are ploughs for the purpose of raking to the thickening zone waste sludge and heavy solid matter such as grit which settles on to the tank floor. The thickening zone consists of a centrally placed conical sludge hopper located below the main floor of the tank in which additional ploughs operate to promote thickening of the sludge and to direct it to the outlet pipe. The entire rotating mechanism is carried on a centre column support.

The overflow passes along open troughs to rapid gravity sand filters, which further reduce the small amount of suspended solids in the treated water. For the removal of the sludge, which accumulates at the surface of the filter beds, they are backwashed once every twenty-four hours with spent sea-water. The treated and clarified water contains an average of 0.005 gm. of suspended solids and 0.06 gm. of dissolved calcium carbonate per litre.

Settling

The reaction mixture from the reaction tanks passes to the settling tanks, which are 185 ft. in diameter, with conical floors falling to a maximum depth of 23 ft. at the centre. The suspension from the reaction tanks enters the settling tanks through ports at water level in the centre column. The settled precipitate of magnesium hydroxide is worked to the centre by conventional raker arms with inclined rakes along the bottom member and the thickened slurry is withdrawn by means of centrifugal pumps situated beneath the tanks, which discharge through rather long pipe lines to the filter house.

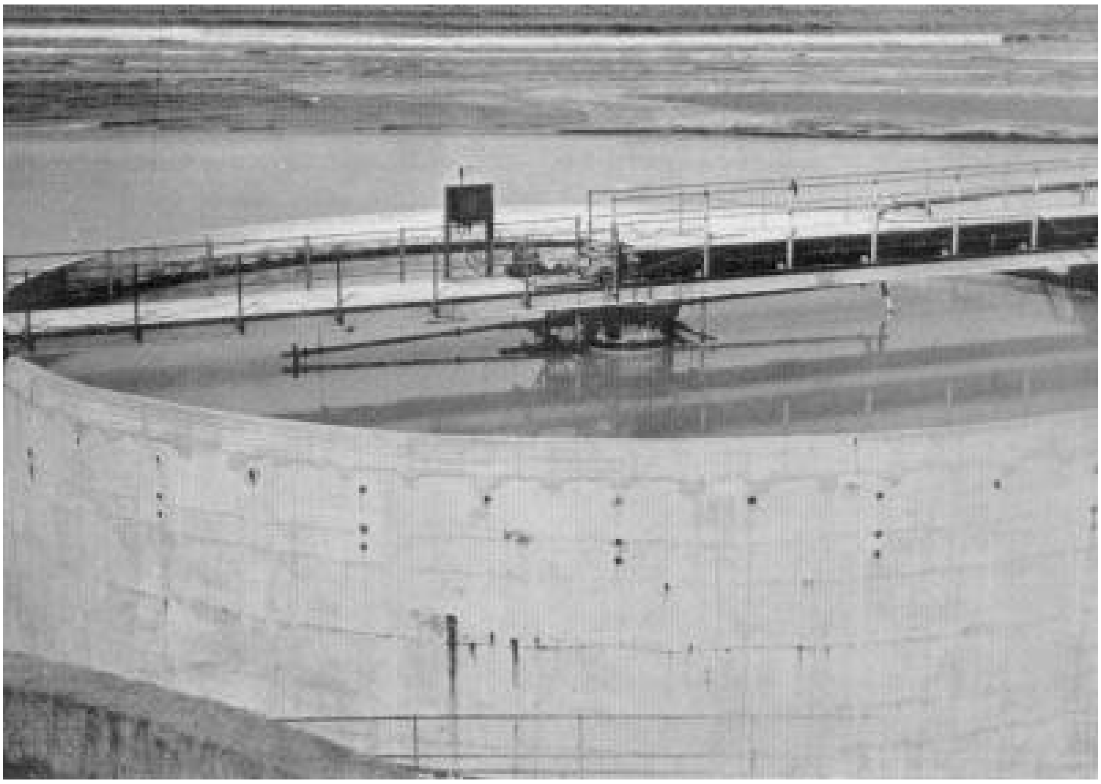
Filtration

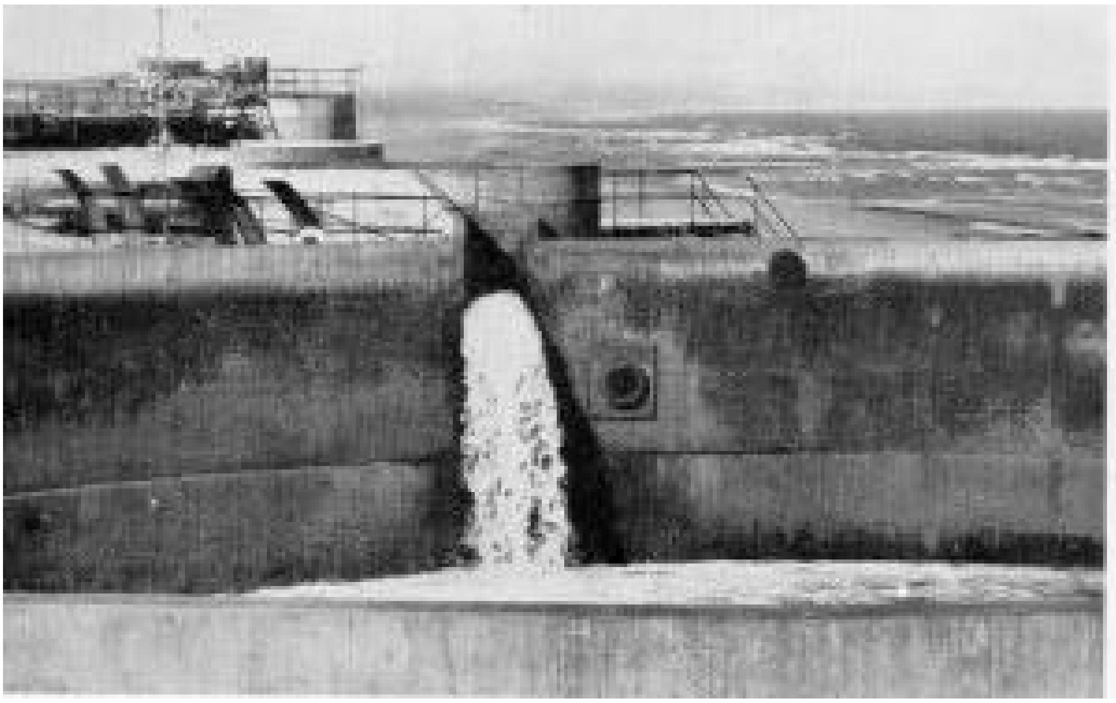
The slurry passing to the filter house contains about 300 gms. per litre of magnesium hydroxide, and while many filtration schemes have been considered, batteries of rotary disc filters were originally installed and have been used in all subsequent extensions.

These have the advantage of economy of floor space, reasonable first cost and the fact that filter cloth bags for individual sectors can readily be made on site; furthermore, there is no particular difficulty in making filters of quite large filter capacity (up to 1,000 sq. ft.) in one unit. Against these favourable aspects must be set the rather complex form of the filter tank, which on one side must leave a space between individual disc troughs to permit the discharged cake to fall away from the filter. Washing on the cloth is not easy to arrange and it is not a simple matter to fit a scraper wire to ensure complete cleaning of the cake from the cloth during the blow-off period.

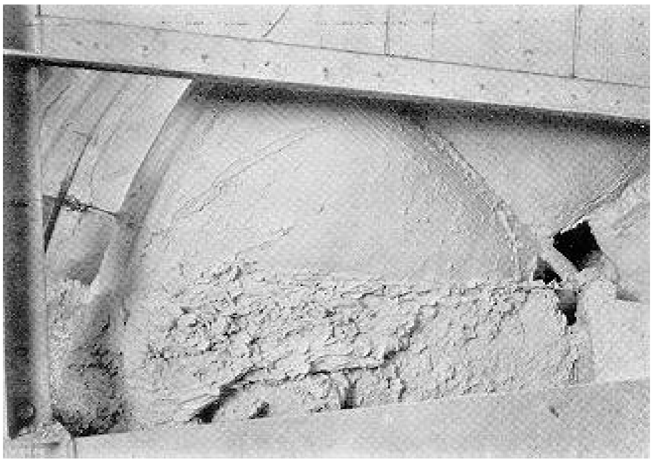
For a production of 700 tons dead burned magnesia per week, a total filtering area of 3,000 sq. ft. is necessary. Experimental work has been carried out on a small filter to determine optimum conditions as to cake thickness and speed for the slurry used at Hartlepool, and it has been found that with a slurry concentration of 300 gms. magnesium hydroxide per litre a ½ inch. cake with a time cycle of 9 1/2 minutes is required.

The *filtrate* from the rotary filters passes via a bottle to pumps which discharge into wash tanks so that the residual magnesium hydroxide which is passed through the filters either accidentally or through the normal porosity of the cloth is not lost but is added to the general stock of slurry. The *cake,* which contains about 33 per cent. magnesium oxide, is carried by means of a belt conveyor to the feed end of the rotary kilns, a distance of some 350 ft. As originally designed, cake from the filters was fed on to a wash belt running the length of the kiln house, but although the wash belt proved unsatisfactory, it had unfortunately determined the relative positions of the filter house and kiln feed hopper. The wash belt has now been dismantled, but nevertheless all filter cake has to follow this route. Maintenance of this long belt conveyor is quite a difficult problem, as also is the complete. removal of the cake from the belt. When it is remembered that the cake has the consistency





The top photograph shows one of the Dorr Hydrotreators, and the lower the raw water storage intake. For ten hours *per diem* these raw water storage tanks are responsible for the supply.



For refractory purposes it is not essential to remove these radicals as they may be volatilized or decomposed during the high temperature calcining operation.

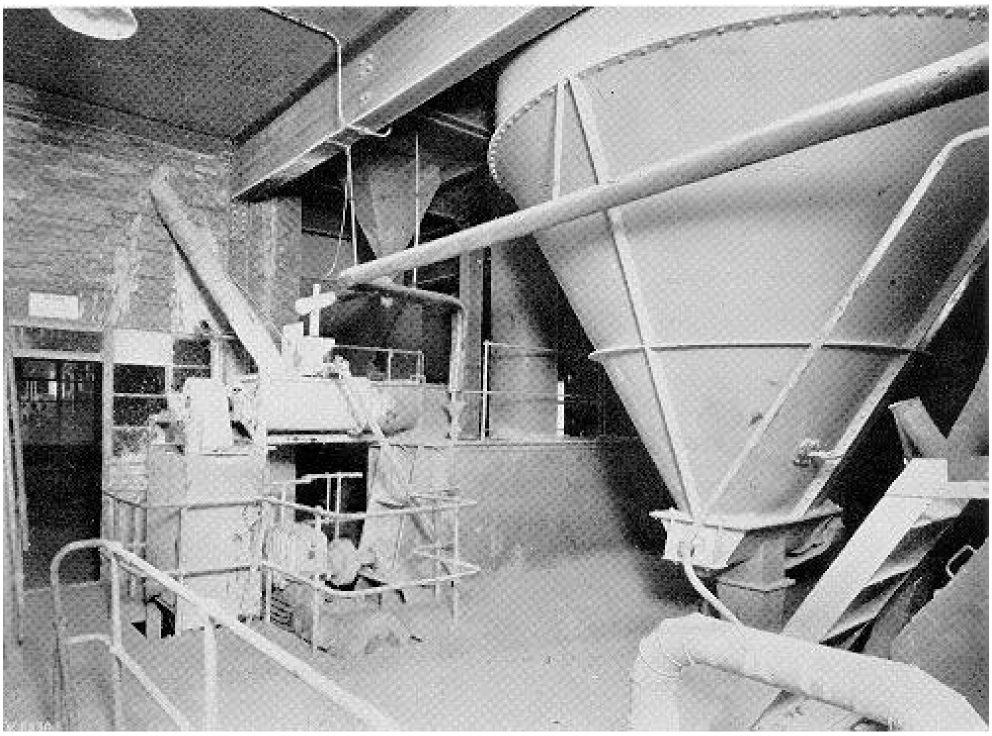
TABLE

Ion.	Conc. in spent liquor gm. ions/litre.	Amount absorbed as % of MgO
Ca^{2+}	6.53×10^{-2}	0.2
Cl^{-}	5.50×10^{-1}	0.8
SO_4^{2-}	2.75×10^{-2}	1.2

During this process, for which rotary kilns are employed, first the free water and then that combined with the magnesium hydroxide is driven off. As the material passes into the hotter zones of the kiln, alkali metal salts are volatized and

Above: An unusual view of one of the rotary vacuum disc filters (although one often sees it like this we do not remember seeing such a photograph before).

Right: The Knibbs-Sturtevant hydration plant.



of a stiff paste it will be appreciated that this removal is not a simple question of scraping. Various devices have been tried but the most satisfactory method, which is now employed, is the use of fine water sprays at the discharge point. This keeps the face of the belt wet and hence helps the scraper to clean the belt completely; it also reduces the accumulation of dried or semi-dried paste on the idler rollers on the return journey.

Settling, Thickening, Washing and Filtering

Chemically these processes taken together effect partial removal of the soluble impurities associated with the magnesium hydroxide. Settling, thickening and filtering do so by reducing the ratio of the liquor to the precipitate, and washing by diluting this liquor and by taking undissolved substances into solution. Of interest from this standpoint is the degree to which various ions in sea-water are absorbed by magnesium hydroxide, the absorption values which are given in the Table indicating that when a substantially chloride and sulphate-free hydroxide is required a counter-current decantation rather than a displacement fresh water washing process should be employed.

carbonates and sulphates are decomposed. Reactions then occur, according to the composition of the calcine, between the acidic and basic oxides while the bulk of the magnesia does not enter into combination but crystallizes in the form of periclase. An average analysis of the refractory product made at Hartlepool is:

SiO_2 --- --- --- --- --- --- --- ---	2.11%
Al_2O_3 --- --- --- --- --- --- --- ---	1.38%
Fe_2O_3 --- --- --- --- --- --- --- ---	1.38%
CaO --- --- --- --- --- --- --- ---	2.70%
MgO --- --- --- --- --- --- --- ---	92.43%

The porosity of the grain is under 15 per cent. and the crystal size of the magnesia about 0.1 min. (X-ray examination).

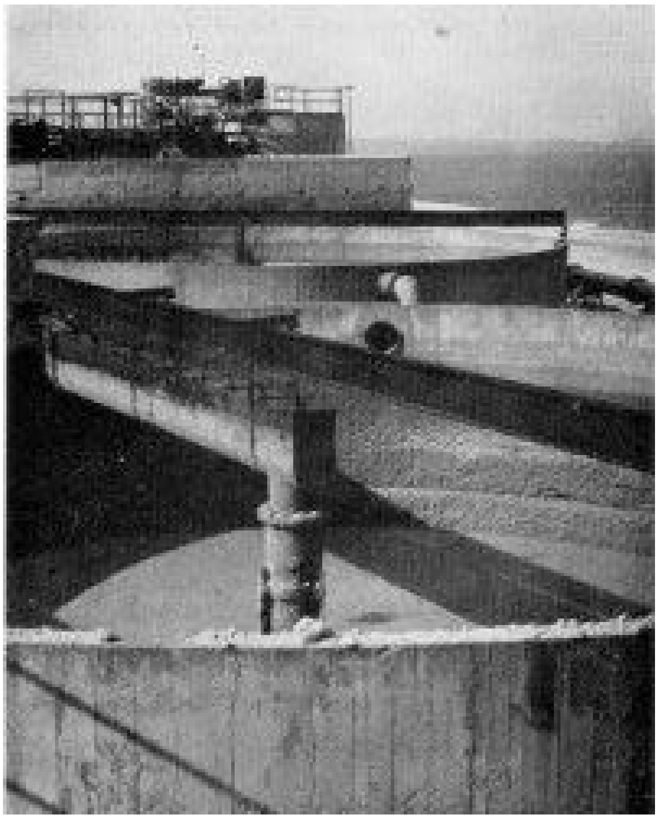
Sea-Water Intake

For a weekly output Of 700 tons 4,000 g.p.m. of sea-water are required. Owing to the flat nature of the beach the pipe lines run 900 ft. into the sea, but even so tides do not permit continuous pumping for more than seven hours. This means that for about five hours each tide or ten hours per day, water for process is taken from a storage tank, and that sufficient pumping capacity has to be installed to cover the low-tide period. Two pipe piers have been built of wood construction carrying a rail track on which small trucks and bogeys can be run for repair work on the pipeline or strum end. The pipelines themselves (four in number) are of bitumen-coated cast iron construction, with semi-flexible joints of the "Victaulic" type. The use of wood for the pipe piers and flexible joints for the pipe lines is rendered necessary by the heavy seas which sometimes occur on the N.E. coast. As alternative materials, steel was excluded on account of cost and corrosion, while reinforced concrete was ruled out by the high cost of a pier sufficiently rigid and robust to withstand storms, bearing in mind that at this part of the coast there is no rock near the surface to give anchorage to steel or concrete piles. Another difficulty, which has not yet reached serious proportions in beach pipe lines, is the growth of mussels; the cure for this is to administer heavy doses of chlorine, but the cost of installing the necessary rubber-covered pipe lines to the extreme end of the piers is a very formidable one. Corrosion of the beach pipelines is not a serious problem and throughout the works bitumen-coated cast-iron pipes are used where possible. Some corrosion does occur where the hard skin is broken, as for example, tapped holes for pressure drop across orifices.

The pipe lines enter the beach pump house some 14 ft. above beach level and the beach pumps discharge into a sand trap which, as its name implies, allows heavy solid suspended matter to separate from the sea-water before passing to the half-tide storage tanks. The sand traps also offer an opportunity to strain out seaweed and similar material, which finds its way into the pipelines. The beach pumps are of conventional centrifugal type and, owing to the extremely long pipe line and hence high suction lift, vacuum priming units are to be fitted for use when the water level is approaching low tide. The half tide storage tanks have flanges fitted near the base for removal of sludge, which, after a period of time, accumulates on the floor. From the half-tide storage tanks the raw sea-water is passed to the hydrotreators for pre-treatment, and thence, after filtration, to reaction.

Materials of Construction

For the sea-water system, bitumen-coated cast iron is the material of choice for pipe lines from the point of view of corrosion. There are obvious disadvantages, however, arising from weight per foot run, fabrication problems, and the rigidity of the completed line. Where temporary runs of pipe are required, mild steel pipe, suitably protected by bitumen coating, can be used. Mild steel is also used for



One of the rapid gravity sand filters. The delivery to it is discussed in the text.

open channels, which are preferred where scale deposition is likely to be serious, as, e.g., for connection from the hydrotreators to sand filters. Scale formation also occurs in pipe lines carrying pre-treated water to the reaction tanks and can be removed by acid treatment with 11 inhibited" hydrochloric acid or manually, dismantling and cleaning each length in turn.

For pumps, the centrifugal type is used throughout the works and experience has shown that a bronze impeller in a cast-iron casing is most satisfactory. The bronze impellers appear to resist corrosion quite well but in the case of pumps handling slurries from the hydration plant or the settling tanks serious erosion occurs.

Storage tanks for sea-water, dolime cream or settled slurry as well as those used for sand filters, reaction and settling are made of reinforced concrete. This material has the merit of resistance to corrosion, permits of rapid construction and does not contaminate the product. Some cases have occurred, however, where penetration into and action with the concrete has taken place and the exact mechanism is not yet known. In one instance a settling tank floor showed penetration, which in places was deep enough to expose some of the reinforcing rods. Investigation suggested that this was due to insufficiently closely graded material used for the aggregate in the original concrete. The affected parts were patched, the whole inner surface of the tank sprayed with liquid cement/ sand mixture under pressure, and finally coated with bitumen emulsion. A second and more recent instance was found in a settling tank which had received a surface dressing of a rich cement/sand mixture. Here the cement had largely disappeared, leaving only a sandy surface.

The third case was of a tank used for storing. settled slurry which, on demolition, revealed distinct softness of the walls. All these instances suggest porosity, absorption and possibly crystallization leading to surface disintegration, and thence further penetration. It is clearly impossible to say at what stage the trouble occurs or how rapidly it proceeds because storage and settling tanks are only emptied at infrequent intervals.

View of one of the rotary kilns with clinker cooler beneath.

PRINTED IN GREAT BRITAIN BY THE ALCUIN PRESS, WELWYN GARDEN CITY, HER-IS,
FOR "FLUID HANDLING", 33 SOUTH AUDLEY STREET, LONDON, W.1

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