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THE USE OF GRAPHITE COOLERS IN THE SULPHURIC ACID INDUSTRY

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The cooling of sulphuric acid dates from the very beginnings of its industrial production. It gives rise to problems posed not only by the material to be cooled but also by the available means of cooling it.

The problems posed by the acid itself, whether diluted or concentrated, nitrated or denitrated, were easily resolved, thanks to the "passive" nature of certain metals (e.g. lead and iron) when in contact with acids. However, the difficulties posed by the method of cooling have proved to be much greater. Subterranean water, river water and sea water are generally used for industrial cooling. In the first two cases difficulties arise from the hardness of the water, the material in suspension and the quantity available. In the case of sea water, the metallic corrosion it caused was the great obstacle to its use. This problem produced particularly disagreeable effects in the Mediterranean area, as for example at the Drapetsona factory in Greece, because of the harmful effect of the various additional factors.

It is well known that the water of the Mediterranean contains from 3.5 to 4.0% of $NaCl + MgCl_2$. Because of the evaporation occurring on the surface of the coolers it is quite possible to obtain a saturated solution or even a deposit of salts on the metallic surface.

The temperature of the sea water varies during the course of the year from 13° to 28° C, so that the effluent water easily reaches 40°C.

Finally, to complete the picture, we should mention the molluscs, seaweed and other mico-organisms, which are deposited in the relatively tranquil parts of the water distribution system, in the sluices, the bends in the pipes and the distributors. Under the influence of a high temperature these organisms can multiply at such a rate as to block the circuit.

The following material was successively used for the construction of coolers at Drapetsona.

1. Lead. Coils made of pure lead were the first cooling elements used for sulphuric acid. The choice arose from the lead chamber process, from which the technique was taken. However, the high degree of nitration encountered in the modern systems of absorption towers (equivalent to as much as 6% HNO_2) and the high concentration of contact process acid (up to 98,5% H_2SO_4) caused lead to be easily attacked. This corrosion is so serious that one can no longer talk of the "passive" nature of this metal.

2. Cast Iron. Cast iron has been widely introduced into the sulphuric acid industry. It is very resistant to highly concentrated, nitrated acids. Unfortunately, it is not similarly resistant to warm Mediterranean sea-water. Even with an average silica content, the life of the cast iron in the coolers is limited. This is exclusively due to the chloride content of the sea water and to its inevitable concentration by evaporation. The truth of this hypothesis was clearly demonstrated by periodically replacing the sea water by fresh water: acid leakages ceased immediately.

Similarly, exact measurements of the internal and external diameters of the pipes in the coolers proved that, whilst the internal diameter, i.e. the acid face, remained constant, that of the external face, in contact with the sea water, continually decreased and, at the same time, became covered with quite a thick layer of corrosion. This layer of corrosion was a con-

siderable obstacle to heat transference through the walls of the cast iron pipes.

3. Acid-Resistant Steel. We tested a series of acid-resistant steels obtained from Germany, Sweden and America. Moreover, measures were taken to prevent the formation of electric cells with other metals. The result was always the same: a great resistance to acid attack, but a serious corrosion by sea water. It was also proved that acid resistant steels have a considerably reduced resistance to highly nitrated acids. The preliminary treatment of these acid resistant steels by a weak solution of nitric acid always promoted their resistance.

4. Glass. This material is undoubtedly resistant to acids as well as salts. It can thus be used without fear of corrosion for the industrial cooling of sulphuric acid. Nevertheless, its sensitivity to pressure and tension discouraged us from using it. In view of similar difficulties which arose in the United Kingdom, the use of glass for this purpose did not seem to us to be very promising.

5. Impregnated Graphite. Graphite has become an important construction material in the development of the chemical industry. Two essential qualities have particularly contributed to this. It is highly resistant to chemical attack and it is an excellent heat conductor. Moreover, its excellent resistance to temperature changes, as well as its electrical conductivity, make it an exceptional conductor of electricity. Graphite has a certain slight porosity, but this can be eliminated by impregnation with acid resistant synthetic resins, and, as is very necessary in the case of coolers, perfect water tightness can thus be obtained.

The essential properties of graphite are given in the following table:

Table 1 - Specification of the properties of graphite

Specific weight	1.8 - 1.9 g/cm^3
Volume of pores	0
Resistance to flexion	300 - 350 Kg/cm^3
Resistance to tension	100 - 170 "
Resistance to pressure	500 - 1000 "
Hardness	35 - 50 "
Heat conductivity	90 - 120 Kcal/m^2/m/H/^{o}C
Electrical resistance	850 - 1400 ohm/cm
Coefficient of expansion	6 - 7.10^{-6} cm/^{o}C

(see Hilliard, "Developments in Graphite Heat Exchangers and Equipment", Industrial Carbon and Graphite, 1958).

The cascade type of cooler, comprising a number of straight pipes with an internal diameter of 80 mm and an external diameter of 100 mm was selected as the most appropriate form. Cubic blocks of graphite are joined hermetically to the ends of the pipe. These blocks enable the direction of the flow of acid to be changed through 90^o and also serve to mount the pipes together. A vertical coil of pipes is formed by the pressure of several pipes mounted together. The acid circulates inside this coil and sea water cascades down the outside.

The first experiments were carried out some ten years ago with experimental miniature pipes and coolers.

To this end we used impregnated graphite from various sources. Although we were quite confident of its resistance to warm sea water, we knew very little about its resistance to highly nitrated acids such as occur in the modern absorption tower systems.

A long and systematic series of experiments finally showed that impregnated graphite can be used, without any reserve whatsoever, for the cooling of nitrated sulphuric acid of 70 - 80% H2SO4 and with a nitrose content of up to 10% calculated as HNO3 36^{o}Bé.

The following details complete the description.

In mid 1958 we installed 78 cooling pipes with a total surface area of about 60 m^2 and another 52 pipes with a total surface of 40 m^2 have been installed since April, 1960. The coolers work continuously. After a further extension in 1962 and early 1963 the total available surface area of impregnated graphite was increased to 160 m^2. During this time we have observed no decrease whatsoever in the thickness of the graphite and there has been no rupture. A few rare leakages have occured, but only at the joints between the pipes and the blocks and between the blocks themselves.

We remedied the former case by first emptying the pipe in question and then applying an appropriate adhesive material. In the second case the leakage was eliminated by using better joints.

Details of the nitrated acids used are as follows:

Acid density at 15°C	58.5 to 61°Bé
Nitrose content as % HNO3 36°Bé	5 to 10%
Temperature of acid on entry	75 to 100°C
Temperature of acid on exit	45 to 55°C
Temperature of sea water, entry-exit, during the summer	27 - 38°C

Heat transference per m^2 of cooling surface, with a pipe thickness of 10mm, was measured on several occasions and was found to be equal to 760 Kcal/m^2/h/° C. This is five to six times greater than for lead. It was even greater than we had foreseen.

The satisfactory results of our experience to date encourage us to extend the use of graphite in our cooling equipment. At the same time, however, we intend to examine the effect on the material of higher degrees of nitration.