International Fertilizer Industry Association

IFA Technical Conference

Edmonton, Canada

12-15 September 1988

PHOSPHORIC ACID EVAPORATION PROCESS IMPROVEMENTS INCREASE PRODUCTION BY UTILIZING A NEW HEAT EXCHANGER CIRCULATING SYSTEM FEATURING A NEW ALLOY

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ABSTRACT

Industria Siciliana Acido Fosforico SpA - an affiliate company of the ENI (Ente Nazionale Idrocarburi) group - operates a world-class phosphoric acid production facility located on the Gulf of Gela in Sicily. Originally built in 1968-1970, this phosphoric acid production plant which utilizes the Prayon process has been continuously improved and expanded to maximize efficiency, increase production and minimize plant outages.

In 1985, the ISAF/Enichem Staff modified two (2) evaporation units by installing a single heat exchanger replacing multiple units in series. A new high capacity, low discharge head axial flow elbow type evaporator pump is the heart of this system. Accordingly, specific attention was directed to the selection of materials for the critically important evaporator circulation pump in design of the two (2) new evaporation circuits. Considerable study and a careful investigation of many materials and system designs were carried out by ISAF-Enichem.

Obviously, the phosphoric acid to be handled has a variable content of corrosive chemicals dependent upon the origin of the phosphate rock. After a deep and through analysis of the liquors to be handled, a slow speed pump featuring a proven nickel chrome alloy of cast-construction for "continuous duty" rating was selected for this demanding duty. Moroccan, U.S.A. and Togo rocks have been handled successfully, with no observed corrosive or mechanical effects on the materials of construction.

Completely trouble-free and maintenance-free operation of both evaporation units since 1985 shows that the material selected and type of construction are very satisfactory. A higher "on-stream" plant performance with lower maintenance and increased evaporation capacity has been achieved. In addition crystalline solid deposits in the heat exchangers have been reduced as a result of the higher acid flow rates design into this modification.

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EARLY HISTORY

Archaeologists confirm human habitation of the Gela area on the South coast of Sicily in prehistoric times. The earliest existence of the town of Gela is directly traceable to the year 690 B.C. After being destroyed by Agrigento's army in the year 290 B.C., Gela rose from the ashes of war to become one of the most powerful cities of the Pre-Christian Greek empire.

In 31 B.C. Virgil commenced writing his world renowned epic "The Aeneid" which details the journey and wanderings of Aeneas. "The Aeneid" features the town of Gela --- "Immanisque Gela Fluvii Cognomine Dicta". To this day, important monuments, walls, and archaeological treasures are preserved in an historical museum atop the highest point in the area.

TODAY

Overlooking the Gulf of Gela, the town of Gela is situated 90 meters above sea level on a rich and fruitful coastal plain nourished by the Gela River. In 1966/1967, Gela became the site for the Industria Siciliana Acido Fosforico SpA (ISAF) phosphoric acid plant facilities. The ISAF plant is located within, and is an integral and important part of the Ente Nazionale Idrocarburi (ENI) petrochemical complex.

ENI's complex comprises a 75,000 BBL/day oil refinery processing crude oil from a number of suppliers. These include oil wells located near Gela in the Sea of Sicily channel as well as other sources. ENI's petrochemical complex refines not only crude oil but also produces olefins, polymers, basic chemicals, and through the ISAF facilities, NPK fertilizers.

SHIPPING TERMINAL FACILITIES

Gela is strategically located convenient to vital supply sources as well as important fertilizer markets. Geographically, Gela enjoys a close proximity to the busy Mediterranean shipping lanes. The shipping terminal and handling facilities at Gela are very efficient and quite impressive. Figures I and II depict the shipping facilities available at Gela.

MATERIAL SUPPLY - PRODUCTION FACILITIES

ISAF's phosphoric acid complex consists of both sulphuric acid and phosphoric acid process manufacturing units. Phosphate rock, originating from a number of areas, is processed at the ISAF complex. Elemental sulphur, initially derived from the famous Sicilian sulphur mines near Gela - is now available from several suppliers. Sulphuric acid is also received from hydrogen sulphide based H_2SO_4 plants (EniChem Agricoltura) located within the ENI refinery complex.

Principal production at ISAF-Gela is phosphoric acid - 43 to 45% P_2O_5 equivalent - which is marketed as NPK solutions.

SULPHURIC ACID PLANT

Sulphuric acid is manufactured at the rate of 550 metric tons per day in a single absorption, sulphur burning H_2SO_4 plant built by Siry Chamon SpA based upon the Chemico H_2SO_4 process. The elemental sulphur burned in this plant is received from Claus sulphur recovery units operating in Sicily.

Sulphur dioxide is removed from the tail gas in an ammonia scrubber to minimize SO_2 emissions to the atmosphere. Heat energy available from the exothermic sulphuric acid process reaction is used to produce steam for the evaporation and concentration of the phosphoric acid.

As indicated earlier, H_2SO_4 production from the 550 T/D Chemico design plant is supplemented with sulphuric acid from two (2) 300 metric ton per day hydrogen sulphide based H_2SO_4 plants (EniChem Agricoltura) operating in the ENI complex. Obviously, minimum handling, close proximity, plus full utilization of usable by-products maximize efficiency at the ISAF-Enichem complex.

PHOSPHORIC ACID PLANT

Phosphoric acid is produced from phosphate rock which originates in the United States of America (Florida), Togo, and Morocco (Kouribga). Occasionally, rock from other sources is utilized, with much of the rock processed being heavily laden with halogen content.

Production of phosphoric acid is at a rate of 400 metric tons per day in the ISAF plant which is based upon the Prayon process. The plant flow sheet consists of two lines of attack tanks, two Bird Prayon filters, and three evaporator circuits such as depicted in Figure III. Please see Figure IIIA for an actual photograph of this system.

The evaporator trains are of the conventional forced circulation type and operate under vacuum. Filtered acid is introduced into the circuit to be concentrated to 43-45% P_2O_5 equivalent value. System components, originally installed in 1967-69 include a cone-bottom flash tank, a process heat exchanger, an axial flow circulating pump, and spray condenser/steam ejector. The flash tank and piping are rubber-lined steel while the shell and tube heat exchangers and evaporator circulating pumps are alloy construction.

While the phosphoric acid plant operates with a minimum staff, preventive maintenance programs are conducted regularly to assure minimum maintenance and production costs. For example, the attack, filtration, and evaporator trains are washed weekly with 5% H_2SO_4 (at 60 degrees celsius). This prevents excessive gypsum build-up and accumulation of phosphate solids which foul heat transfer surfaces and also increase system's flow resistance. Major shutdowns for maintenance of two to three weeks duration are scheduled once during every two years of operation.

EVAPORATOR MODERNIZATION PROGRAM

An evaporator modernization program was undertaken starting in 1983 and completed in 1985. This program principally involved replacing multiple heat exchangers installed in series on two of the three evaporator circiuts.

In each case, the series installations of heat exchangers were replaced by a new single shell and tube heat exchanger of alloy construction. The new heat exchanger consists of 450 tubes which are 6265 mm long x 34 mm I.D. and mounted in the vertical position. Phosphoric acid is heated by saturated steam at two (2) bars absolute pressure available from the sulphuric acid plant (ISAF) and from the power station.

INITIAL EXPERIENCES FOLLOWING MODERNIZATION

Shortly after start-up of the revamped evaporator circuits, several problems occurred which later proved to be related.

1. A) The six (6) existing shell and tube graphite heat exchangers required frequent maintenance and provided unsatisfactory "on-stream" performance.

   B) The six (6) graphite heat exchangers were replaced by two (2) stainless steel heat exchangers.

2. Heat transfer surfaces in the stainless steel exchangers were becoming fouled with crystalline solids at frequent intervals requiring extra maintenance.

3. Corrosion and vibration were observed within the axial flow circulating pump. These pumps were fabricated lightweight sheet alloy and were suspended in the piping without any other foundation support.

4. The fabricated propeller of the sheet metal alloy evaporator circulating pump completely lost a blade which broke off at the propeller hub.

In summary, production rates were unacceptable and numerous outages for pump repairs were being experienced.

IMPROVEMENTS - LEWIS LEWMET ALLOY PUMPS

After careful study, ISAF management concluded that many problems could be solved by replacing the evaporator circulating pumps with heavy duty axial flow pumps of more rugged construction and with improved hydraulics. Pumps of cast construction were preferred based upon the previous poor experience with lightweight fabricated sheet alloy pumps. Moreover, an alloy having both corrosion and erosion resistance to phosphoric acid produced from multiple rock sources was critically needed. Additionally, this alloy should resist the corrosive attack of the periodic "flushing" with 5% sulphuric acid used for de-scaling purposes. Finally, increased flow rates reduce the tendency for crystalline solids to foul the heat exchanger surfaces.

Lewis axial flow elbow-type pumps with heavy wall cast elbows and propellers cast in one piece were selected. All component parts of these pumps are ruggedly constructed and each pump is securely mounted on its own sturdy foundation to provide smooth, reliable operation. Figure IV shows this installation. Wetted parts are cast of LEWMET 25 alloy - a proprietary superalloy developed specifically for phosphoric acid evaporator circulating pumps in high temperature, high chloride/fluoride applications (See following section on Metallurgy).

In addition to rugged, cast components and superior metallurgy, the Lewmet alloy pumps have the following mechanical features: Figure V shows a cross-section view of this pump.

1. Separate casing and elbow construction to provide for easy alignment and for the simple installation of a replaceable wear resistant casing liner when required. The replaceable Lewmet alloy liner allows renewal of the original manufacturing clearances and original performance as specified.

2. Precision bearing frame alignment is maintained with self-aligning rabbetted fits which assure vibration free operation. Heavy duty bearings and shaft insure mechanical reliability.

3. LEWMET alloy shaft sleeve, centrifugally cast and hardened to 450-500 Brinell, extends stuffing box service life. The Lewmet alloy shaft sleeve protects the pump shaft from normal packing wear and erosion in the stuffing box area.

4. Contoured propeller nut sealed with elastomeric O-rings for optimum hydraulic efficiency.

The pumps selected have 600 mm diameter suction and discharge flanges and are rated for flows of 3600 cubic meters per hour at a head of 4 meters liquid column. They are driven through a multiple vee belt drive at a conservatively low speed of 510 rpm, minimizing impeller velocity at the propeller inlet. This enhances NPSH characteristics and greatly reduces possible abrasive and corrosive wear.

Performance of the evaporator system improved immediately upon installation of the Lewis pumps. Higher acid flow rates increased heat transfer with longer operating periods between descaling operations resulting in higher production capacity. The pumps run smoothly and show no corrosion or erosion upon routine, periodic inspections.

METALLURGY

Wet process phosphoric acid presents a particularly demanding environment for metallic corrosion resistant materials. While chemically pure phosphoric acid is only mildly corrosive, wet process acid is highly corrosive, primarily due to the presence of halogen impurities which originate in the phosphate ore. The corrosive characteristics of the wet process acids will vary depending upon the phosphate ore source and the levels of impurities associated with the particular ore. The problem is further aggravated by the presence of solids, primarily gypsum and siliceous gangue.

Evaporator pump circulation duty represents an especially difficult application for a corrosion resistant material. In addition to corrosion, the pump material is exposed to erosion and high local velocities. Previous operating experience using commercially available materials of construction for evaporator pumps had demonstrated that these materials possessed only moderate resistance to corrosion and erosion, especially for the higher velocity components. The need for a highly corrosion resistant alloy was apparent.

MATERIALS REVIEW

A review of materials used historically in pumping equipment for this service was undertaken as a first step in developing a premium corrosion resistant alloy. As expected, considering the environment, maximum life was obtained from materials having high levels of chromium and molybdenum. A summary of commonly used materials is shown in Table 1.

It was also evident in reviewing prior operating experience that many failures were related to fabrication and welding deficiencies. Premature failures were associated with cracking, pitting, intergranular corrosion, and poor quality workmanship. The severity of this duty is magnified by the complexity and inter-relationship of the system components, shown in Figure III.

The final criteria for selecting a premium alloy for this duty is therefore summarized as follows:

Corrosion Resistance - the alloy must be resistant to wet process acid, even at the highest levels of halogen impurities. The alloy must also be resistant to 5% H_2SO_4 used for descaling.

Erosion Resistance - the alloy must resist the attack of the acid under relatively high velocity conditions.

Abrasion Resistance - the alloy must resist the abrasive attack of the entrained solids not removed in the filtering process.

Ease of Manufacture - the alloy should be readily castable using proprietary available foundry equipment and techniques at economical costs.

In the search for an improved alloy for phosphoric acid service, attention focused on LEWMET, a nickel-cobalt-manganese alloy material, which is well known in the fertilizer industry for its application in high-velocity wear components used in sulphuric acid tower circulating pumps and valves. Specifically, LEWMET 55 makes use of a complex austenitic matrix and contains a hard second phase rich in molybdenum and silicon that is beneficial in abrasive and strongly oxidizing acid streams.

CUSTOM DEVELOPED ALLOY

In order to adapt LEWMET 55 alloy for phosphoric acid applications, modifications were necessary to resist fluoride attack by eliminating the alloy second phase. The object was to produce a totally austenitic single phase material having maximum chromium and molybdenum content.

Considerable experimental work was required to define the maximum levels of chromium and molybdenum that could be sustained in a fully saturated condition.

Concurrent with alloy development work, actual production castings were produced to determine casting parameters. Suitable welding electrodes and welding techniques were developed at the same time.

The resulting alloy, designated LEWMET 25 (Table 2), was introduced commercially in 1981 for evaporator pump service and met the original criteria for corrosion resistance, abrasion resistance and castability.

CORROSION TESTING

As part of the original review process for the ISAF modernization, an extensive corrosion testing programe was undertaken by the ISAF engineering/plant personnel. Selection of proper materials of construction for the major components was considered to be critical, dueto the usage of various phosphate ores. Detailed analysis of the three ores presently in use are shown in Table 3.

Original testing was performed in 1983, on acid produced from Bou Craa rock from Morocco. Additional testing was performed in 1985 on acid produced from Khouribga rock. Test restuls are summarized in Table 4. Acid analyses are summarized in Table 5. In both tests, LEWMET 25 was found to provide the lowest corrosion rates of all materials tested. In fact, the corrosion rate of LEWMET 25 was found to be significantly lower than all other alloys tested.

The corrosion test results for LEWMET 25 have now been confirmed by actual operating experience. Specifically, after almost three (3) years service, no evidence of corrosion, abrasion, or erosion has been observed on the original pumps.

SUMMARY

The new pumps have operated free of maintenance throughout three years. In additon, heat transfer in the heat exchanger and longer operating runs between descaling operations have increased instantaneous and long term production capacity. This is a classic example of how correctly selected pumps and superior materials can lead to improved overall plant operation.

TABLE 1

EVALUATION OF ALLOYS MATERIALS COMMONLY

USED IN PHOSPHORIC ACID SERVICE

(NOMINAL PERCENTAGES)

	CHROMIUM	MOLYBDENUM	CHROMIUM + MOLYBDENUM TOTAL	MATRIX STUCTURE
LEWMET 25	29	4.5	33.5	Austenitic
LEWMET 15	28.5	2.25	30.75	Duplex - Austenitic & Ferrite
SANICRO	27	3.5	30.5	Austenitic
CD4MCu	26	2	28	Duplex - Austenitic & Ferrite
FERRALIUM	25	2.5	27.5	Duplex - Austenitic & Ferrite
HASTELLOY G	22	6.5	28.5	Austenitic
INCOLOY 825	21.5	3	24.5	Austenitic
JESSOP 700	21	4.5	25.5	Austenitic
CARPENTER 20 Cb-3	20	2.5	22.5	Austenitic
ALLOY 20	20	2.5	22.5	Austenitic

Note: 1) The above table ranks alloys according to chromium plus molybdenum content in descending order from top to bottom.

2) Trademark ownership of above materials shown on Table 2.

TABLE 2

LEWMET 25(R)

NOMINAL CHEMICAL COMPOSITION

Element	Weight Percent
Carbon	.05
Silicon	.50
Manganese	3
Chromium	29
Nickel	38
Molybdenum	4.5
Copper	3
Cobalt	6
Iron	15

MECHANICAL PROPERTIES

Yield strength - psi	38,000
Tensile strength - psi	70,000
Elongation - %	55
Reduction in Area - %	60
Brinell Hardness	146

(R) Registered trademark of Chas. S. Lewis & Co., Inc. U.S.A.
Patents issued in the United States and other countries.

TABLE 3

TYPICAL ORE ANALYSES

Source:	Togo	Morocco (Khouribga)	Florida
% BPL	70/80	71/72	70/72
% Ca O	51/52	48/50	49/50
% P2O5	36.0/36.2	32/33	32/33
% H2O	1.8/2.0	1.2/1.5	1.2/1.5
% F	3.8/4.0	3.9/4.0	3.8/3.9
% Si O2 (Total)	3.7/3.8	2.4/2.7	4.5/5.0
(Soluble)	1.5/1.6	0.8/0.9	1.4/1.6
% Fe2 O3	1.3/1.35	0.14/0.17	1.3
% Al2 O3	1.1/1.2	0.4/0.45	1.4/1.5
% Cl	.05/.06	.025/.027	.015/.016
% Mg O	.07/.08	.26/.30	.35/.40
% CO2	3/3.5	5/6	3.5/3.6
% SO4	.35/.40	2.4/2.6	1.4/1.5
% Organics (as Total C)	.3/.4	.35/.45	.4

TABLE 4

LEWMET 25 - PLANT CORROSION TEST RESULTS

Location	Khouribga (70 BPL)	Bou Craa (80 BPL)
Reaction Vessel Slurry 32% P_2O_5 - 65/70°C	0.0097 (0.4)	0.011 (0.4)
Filter Acid (Agitated) 32% P_2O_5 - 45/50°C	SAMPLE LOST	0.0026 (0.1)
Product Acid (Agitated) 45% P_2O_5 - 45/50°C	0.011 (0.4)	0.016 (0.6)

TABLE 5

TYPICAL ACID ANALYSES

	Product	Filter
% P_2O_5	43/45	26/30
% F (Total)	0.9/1.7	1.5/2.0
% Cl	0.05/0.08	0.03/0.1
% SO_4	3.2/3.5	2.2/2.5
% SiO_2	0.6/0.7	0.2/0.35
% Fe_2O_3	0.6/1.2	0.2/0.35
% Solids	/0.5	0.5/1.0

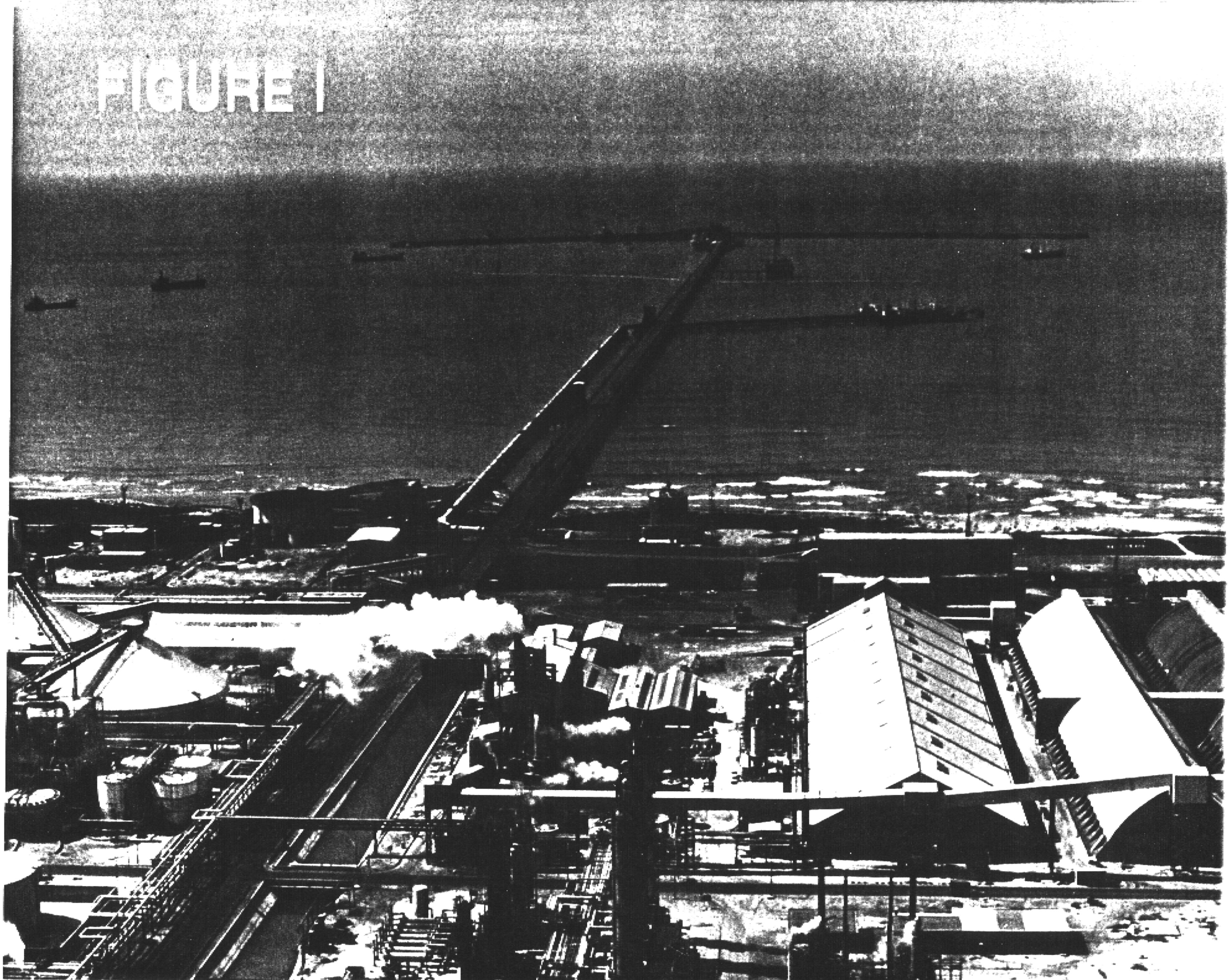


FIGURE I

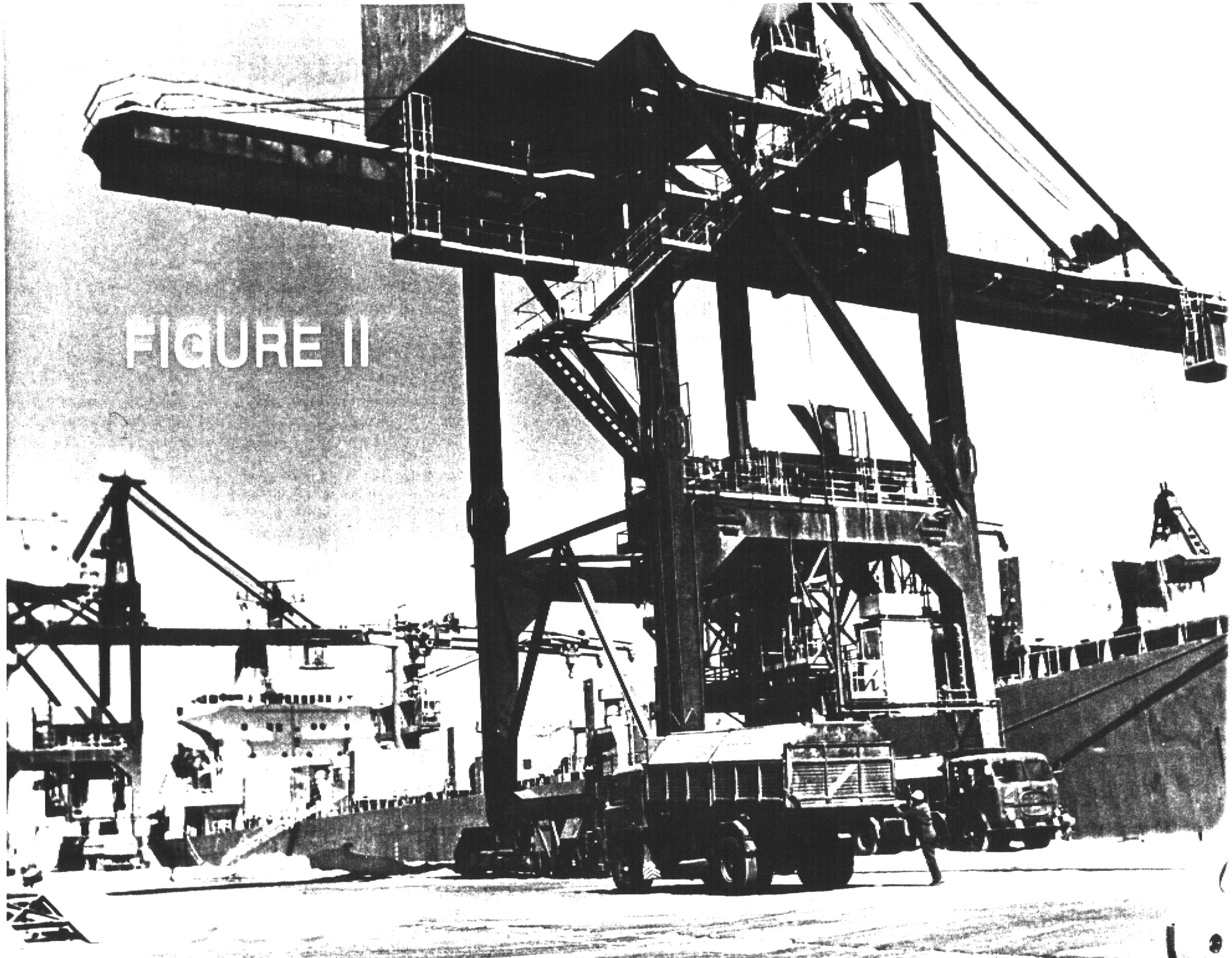
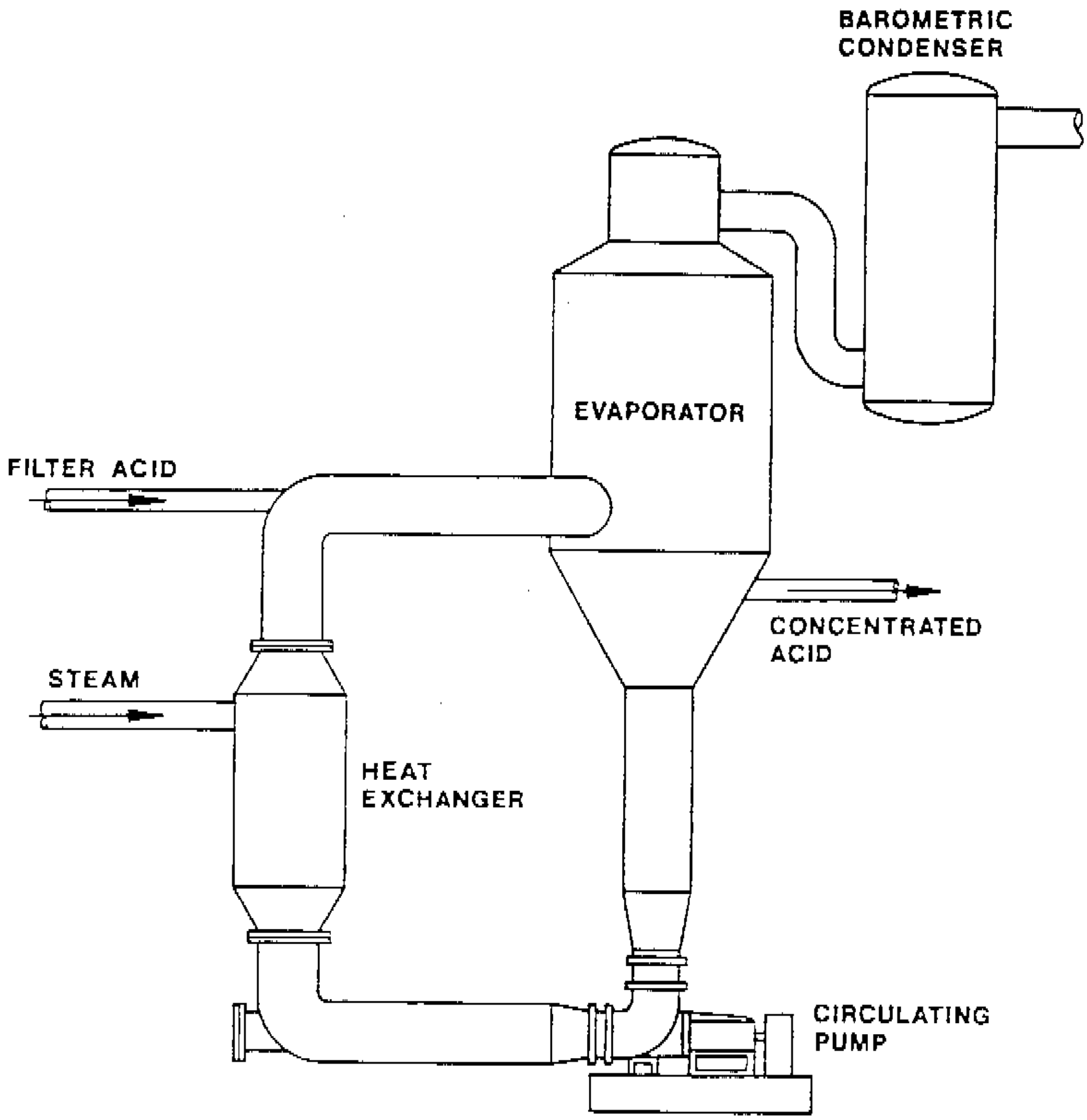


FIGURE II



FORCED CIRCULATION EVAPORATOR

FIGURE III

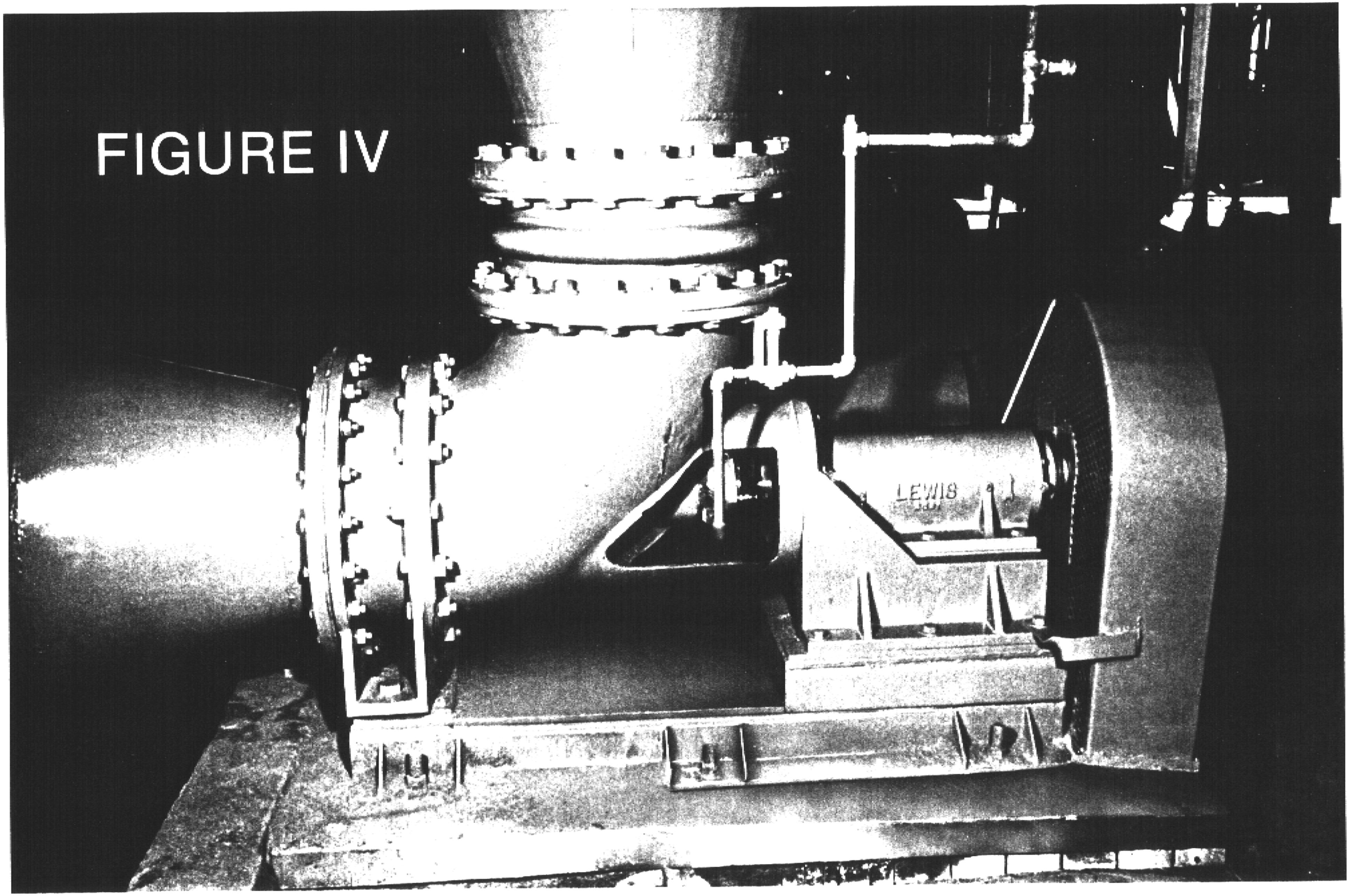


FIGURE IV

TA/88/19 Phosphoric acid evaporation process improvements increase production by utilizing a new heat exchanger circulating system featuring a new alloy, by W. Conti, Industria Siciliana Acido Fosforico SpA, Italy and R. Boillat, Chas. S. Lewis and Co.Inc., USA

DISCUSSION (Rapporteur Mr. A. Davister, Prayon, Belgium)

Q - Mr. R. BARUT (Norsk Hydro Azote, France)

Have you measured corrosion rates for LEWMET 25 in phosphoric acid produced from Togo ore having the highest chlorine content ?

A - At the time of industrial testing, we did not use that particular rock, but in the lab test, we have tested acids with concentration of Cl up to 1200 ppm with corrosion rates less than 5 mils per year.

Q - Mr. P. ORPHANIDES (Duetag, France)

1/ What is the material used for the construction of the metallic evaporator heat exchanger ?

2/ Have you any scaling problems ? Is it still necessary to clean these scalings by so-called boil-out ? What is the chemical nature of the scalings ?

A - 1/ Alloy is SANICRO 28

2/ Yes, boil-outs (65° C, 5% H_2SO_4 solution washing by means of recirculation) remains necessary, but less frequently than before. Let us say once per week to once per ten days pending on the type of phosphate rock used. The scaling is made of gypsum and other solids.

Q - Mr. M. ALOUANE (Industries Chimiques Maghrébines, Tunisie)

1/ The first modernization actions aimed at the substitution of graphite heat exchangers by alloy-type exchangers. It is due to the bad quality of graphite exchangers or for maintenance reasons ?

2/ What are the concentration limits of the acid concerning sulphide, chloride and fluoride that are acceptable for LEWMET 25 ?

A - 1/ The substitution main reason was to reduce maintenance.

2/ We do not know exactly what are the practical limits, because in industrial operation we never reached these limits, as our alloy has always performed satisfactorily. In the lab, some tests with acid containing up to 10 000 ppm Cl^- were acceptable.

Q - Mr. P. BECKER (Duetag, France)

1/ What units are used for corrosion levels in table 4 ?

2/ What is the liquid velocity in the heat exchangers ?

A - 1/ Units are mils per year

2/ Velocity is 2.4 m/sec.

Q - Mr. V. HORKKO (Kemira Oy, Finland)

.../.../...

1/ What are the cleaning intervals of the heat exchangers after installing the LEWMET pumps ? What is the on-stream factor ?

2/ What is the solids content of the concentrated acid ?

A - 1/ Intervals between cleanings : 6 to 10 days pending on rock.

On-stream factor after three years operation is 90-93%.

2/ Solids content os 2 to 3%.

Q - Mr. M. BARLOY (Krebs, France)

1/ What is the cost of LEWMET 25 compared to existing alloys like Ferralium, Sanicro 28, Alloy 20...?

2/ What is the difference between LEWMET 15 and chromium containing cast iron manufactured in France by Creusot-Loire for 15 to 20 years ?

A - 1/ LEWMET alloys contain more than 85% of alloying (non-iron) metals, so they must be more expensive and we can say that MEWMET 25 is 10-15% more expensive than LEWMET 15.

2/ I do not know that Creusot-Loire alloy.

All I can say is that LEWMET 15 is an alloy developed on the basis of research results of an American laboratory.

Q - Mr. N. ROBINSON (Norsk Hydro Fertilizers, U.K.)

1/ How important is nickel in giving resistance to chloride corrosion ? Is there a minimum level ?

2/ What sort of corrosion rates would be expected at temperature of 100°C ?

3/ What is the erosion resistance of LEWMET 25, say in comparision with Ferralium, which has been developed specifically to resist erosion, but has not a very good resistance to chlorides ?

A - 1/Ni is the base metal of this alloy and it has a better corrosion resistance than iron. But, as the acid gives oxidizing conditions, there is a specific corrosion by halogens, that is called "pitting". For that reason, cobalt and molybdenum are added to fight that "pitting" corrosion. Nickel is only used to balance it and serves to obtain a fully austenitic phase.

2/LEWMET has operated safely at GELA at temperatures between 65 and 80° C. In another plant, we have pumps operating for 7 years on 54% P205 acid and 110° C.

3/ THe erosion resistance is excellent; it is so good that machining is difficult and tools have a hard work.

For instance, with a tip speed of 25 m/sec., we have no trace of erosion after three years.