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NEW DEVELOPMENTS IN CORROSION RESISTANT MATERIALS FOR FERTILIZER ACIDS

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ABSTRACT

Fertilizer producers today employ process technology based upon handling intermediates such as Nitric Acid, Phosphoric Acid and Sulphuric Acid. Experienced operations and process people recognize the critical importance of handling these corrosive liquids with safety, reliability, and economy. All too frequently the whole production process must be stopped and shut down because of excessive corrosion and the premature failure of a process pump or control valve.

Within the fertilizer industry, handling nitric acid or liquid ammonia is not a major problem since acceptable service life is obtained with commercially available ordinary stainless steel materials which are quite satisfactory for these requirements. However, phosphoric acid and sulphuric acid production both present serious problems to the plant operator and a challenge to the equipment manufactured in selection of appropriate materials of construction. Obviously, economics and service life are significant factors in the choice of proper materials.

Wet process phosphoric acid is highly corrosive due to the presence of numerous impurities, the most detrimental of which are chlorine and fluorine. Halide impurities typically originate with both the phosphate rock and the wash water used to beneficiate the phosphate rock and can result in unacceptable corrosion rates. Thus, custom tailored corrosion-resistant alloys have been developed specifically for the difficult phosphoric acid intermediates.

Concentrated sulphuric acid used to digest phosphate rock is normally very corrosive. However, process technology in the last 20 years has trended toward ever higher acid stream temperatures to maximize energy recovery from the sulphuric acid process. Higher acid temperatures, coupled with larger scale plants and improved reliability and safety standards have resulted in greater use of premium alloy materials in sulphuric acid production.

Accordingly, increased emphasis upon the use of proper materials of construction is worth consideration by all fertilizer producers. This paper reports upon new materials developments complete with corrosion experience from both laboratory test and actual plant service.

INTRODUCTION

This discussion is necessarily confined to materials used for construction of pumps and valves used in "Strong Acid" circulation duty. Obviously, vessels and piping represent another whole "materials world" to consider. Typically, however, operations and engineering people recognize the primary circulating pumps as the "Heart of the Plant" and compare their importance with the function of the human heart. Thus, in selective materials, the critical nature of circulation pumps/valves must not be overlooked since high acid flow velocities and relatively close running clearances are invariably involved.

SULPHURIC ACID PRODUCTION/MATERIALS

The development of materials of construction for handling concentrated hot sulphuric acid circulated in today's absorbing and drying towers is portrayed chronologically in Figure 1. Typically, tower circulation system pumps and valves must resist sulphuric acid corrosion as well as erosion/abrasion from brick chips and fragments of saddle packing suspended n the sulphuric acid being circulated. This requirement for hardened parts to resist corrosion/erosion/abrasion led to the development of the LEWMET$^{(R)}$ series of alloys which provide hardenability along with superior corrosion resistance in concentrated sulphuric acid duty.

Economics and logistics of spares/maintenance requirements further dictate that materials used for sulphuric acid tower circulation pumps and valves should tolerate a range of acid concentration levels. In actual production, drying towers may not always operate at the specified design concentration. Likewise, acid concentration levels in the absorbing tower/pump tank dilution systems frequently vary from the design level. Inventory cost of necessary spare parts dictate the use of the same material for both 93 and 98% acid concentration duty. Fortunately, LEWMET$^{(R)}$ alloy exhibits acceptable corrosion rates at acid concentrations as low as 80% at temperatures typically encountered in current process streams.

Fluid handling equipment presents a most demanding requirement for corrosion resistant materials. Centrifugal pump components, in addition to being exposed to corrosive process fluids, are subjected to operation velocities approaching 30 m/sec under highly turbulent conditions. The maintenance of close dimensional clearances is necessary to insure maximum hydraulic performance and efficiency. Alloys must possess corrosion, erosion, and galling resistance.

Sulphuric acid plants today typically handle circulating acid strengths from 93% to 99.5% at a maximum temperature of 220°C. The corrosion resistance of alloys within this relatively small concentration range will vary widely. This behavior is attributable to the oxygen solubility in sulphuric acid versus concentration, which decreases rapidly from 99% concentration to 70% concentration.

In general, alloys possessing high levels of oxidation resistance provide maximum corrosion resistance in these applications. Alloying elements which promote oxidation resistance include chromium and silicon. The addition of alloying elements such as molybdenum and copper will improve corrosion resistance in mildly oxidizing environments and those containing reducing impurities. The balance of alloying elements are generally included to control the metallurgical and mechanical properties of the final alloy.

Chromium-Molybdenum alloys are normally selected for use in 93 to 98% H_2S0_4 at temperatures to 140°C. These alloys depend upon the development of a tightly adhering, crack-free, complex oxide film for corrosion resistance.

As shown in Figure 1, the use of highly corrosion-resistant alloys in sulphuric acid dates to 1925, which is roughly equivalent to the commercial availability of these alloys. An early alloy, Illium$^{(R)}$G, had a corrosion rate of less than 0.25 mm/y in 98% H_2S0_4 to 90°C with operating velocities to 30 m/sec. The alloy is fully austenitic and, therefore, susceptible to galling and abrasive wear.

Alloy 20, Fe-20Cr-30Ni-3Mo-3.5Cu, was introduced in 1940. Corrosion rates in 98% H_2S0_4 at temperatures in excess of 90°C and operating velocities above 8 m/sec accelerate rapidly. Alloy 20 is also fully austenitic.

A number of alloy modifications were made over the years, culminating in the introduction of LEWMET$^{(R)}$ 55, Ni-31Cr-3Si-3Mo-3CU, in the early 70's. Corrosion rates are shown in Figure 2. These rates are unaffected by operating velocities to 30 m/sec. The alloy can be age-hardened to 500 BHN, with no loss in corrosion resistance. The photograph in Figure 3 shows a dramatic comparison of 98% sulphuric acid attack upon a LEWMET$^{(R)}$ 55 wear ring and an impeller of a predecessor alloy operating at 110°C.

The mid 1980's saw the introduction of a number of high silicon stainless steel alloys, nominally Fe-18Cr-18Ni-5Si. These alloys possess good corrosion resistance in 98% sulphuric acid at temperatures to 140°C; however, corrosion rates increase rapidly with decreasing acid concentration and with concentrations in excess of approximately 99.5% and into the oleum ranges[1]. These alloys find little application in pumps and valves because of their limited capability, acid concentration-wise.

Chromium-alloyed materials are selected for use in high temperature heat recovery service, 98.0 and 99.5% H_2SO_4 with operating temperatures of 200°C[2]. Alloys used include high chromium austenitic, ferritic, and duplex stainless steels. Again, a minor decrease in acid concentration will cause high corrosion rates, especially under high velocity conditions.

Cast iron has been used in concentrated sulphuric acid for many years. Today, cast iron, ductile iron, and a number of specialty irons continue to be used with good success in this service. Lewis Process Iron, in use since the late 1930's, and L-14$^{(R)}$ Iron, introduced in the mid 80's, are used for pump components where maximum dimensional stability is not required for hydraulic performance. Parts include pump casing, discharge elbows, and discharge pipes. L-14$^{(R)}$ Iron has approximately 60% improved corrosion resistance compared to Process Iron at 132°C.

PHOSPHORIC ACID MATERIALS/DEVELOPMENTS

In the early 1960's Lewis built both 100-MM and 200-MM size cantilever-shaft vertical pumps for phosphoric acid slurry service in "attack" tank filter feed duty. A number of these pumps have been operated with good success for over twenty-five (25) years by phosphate fertilizer leaders in their Port Maitland, and Marseilles, Illinois facilities. Both LEWMET$^{(R)}$ and Illium$^{(R)}$ (Illium$^{(R)}$ is a forerunner of today's LEWMET$^{(R)}$) series of alloys developed by Lewis' metallurgical consultant, Mr. Tom Johnson, were featured in these pumps.

A new generation of Lewis' cantilever-shaft vertical pumps for phosphoric acid filter feed/filtrate duty, introduced in 1980, is shown in Figure 4. This pump design features critical components of LEWMET$^{(R)}$ and externally adjustable impeller/suction plate clearances to maintain hydraulic efficiency in both corrosive and abrasive applications. This design was first developed for Triomf Fertilizers at Richards Bay, South Africa, who were confronted with handling "Very Dirty" molten sulphur laden with volcanic ash, diatomoceous earth, filter oil and "tramp" materials accumulated in overseas shipping and extended storage. More recently, development of two new LEWMET$^{(R)}$ alloys spurred the use of this pump design into phosphoric acid applications having higher levels of halogen contaminants.

Pure phosphoric acid is produced at strengths of approximately 30% P_2O_5 and 42% P_2O_5, depending upon the process technology. Reaction temperatures are normally 70°C (160°F). After filtration, the acid is concentrated to 54% P_2O_5 and 70% P_2O_5 in a forced circulation evaporator.

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Chromium-molybdenum alloys are widely applied in this service. Cast and wrought 316, 317, and Alloy 20 stainless steels have been used for many years. A summary of corrosion rates is shown in Table 1.

Cast duplex stainless steels have been used successfully for many years. LEWMET$^{(R)}$ 15, Fe-28Cr-2.5Mo-3.5Cu, was introduced in the late 1950's; chemical composition is balanced to eliminate the possibility of sigmaphase, and Fe-Cr intermetallic, which causes embrittlement and a large increase in corrosion rates in this environment. Corrosion resistance is shown in Table 1. This alloy is used extensively even today, as shown in Figure 5, which highlights a 750 MM pump supplied to a Florida producer in 1992. Wrought duplex stainless steel alloys are now readily available from a variety of sources. The duplex stainless steels provide the added benefit of improved abrasion resistance due to the higher hardness and strength which is a result of the austenitic-ferritic microstructure. Chemical and mechanical properties of LEWMET<190> 15 are summarized in Table 2.

A variety of modified Alloy 20 type alloys are available in both cast and wrought form. Generally, these alloys have increased molybdenum content of 4.5% to 6%. Corrosion rates are summarized in Table 3.

LEWMET$^{(R)}$ 25, Ni-29Cr-4.5Mo-3Cu, was developed in the late 70's in conjunction with a Florida producer for use in evaporator service[3]. Previous operating experience at this site had shown that the lives of commercially available alloys for evaporator pumps were less than desired. Process changes were therefore implemented to improve production rates since the need for an alloy with superior corrosion resistance was imperative to minimize maintenance outages.

Development work was directed at producing an alloy having high chromium content to provide a tough, corrosion-resistant film and sufficient molybdenum to enhance the formation of the protective film and provide resistance to pitting. Based on prior materials experience, a molybdenum content of 4.5% was arbitrarily chosen. A copper content of approximately 3% was determined as optimum based on historical testing and operating results. Silicon content was reduced to 0.5 to 0.75%, the lowest value consistent with good foundry practice, to maximize corrosion resistance in the presence of fluorine compounds. Chromium content and the balance of all other alloy and residual elements were varied to provide a fully austenitic microstructure.

Earlier development work in producing a fully austenitic nickel base alloy for concentrated sulphuric acid service was used as a starting point. LEWMET$^{(R)}$ 66, Ni-3Mn-6Co-31Cr-3Si-3Cu, had shown that a Ni-Mn-Co matrix, as opposed to a wholly nickel matrix, would allow higher levels of body centered cubic alloying elements.

An empirical calculation method, which was derived during previous experimental work, was used to develop an analysis rich in body centered cubic alloy which, after solution annealing, would be fully austenitic. The calculation entails the summation of the atomic percentage of FCC and BCC alloying elements. A ratio of total BCC to FCC alloying elements of less than 0.9 will result in an essentially fully austenitic structure for this alloy group.

A 100 Kg. experimental heat was melted to the calculated analysis and poured into test bars. High temperature solution annealing of the test bars was completed. The original analysis was found to contain approximately 5/10% of a high alloy second phase. A scanning electron microscope equipped with EDAX capabilities was used to identify the chemical analysis of any second phase. Base alloy chemical analysis was modified and the process was then repeated.

A relatively small number of heats resulted in the final analysis, Ni-3Mn-6Co-29Cr-4.5Mo-3Cu. Nominal chemical analysis and mechanical properties of LEWMET$^{(R)}$ 25 are summarized in Table 2. Corrosion rates are summarized in Table 3. The three original pumps have now been in service for approximately nine years and the major alloy components are still in good condition.

In 1986, two 600-mm axial flow propeller pumps of LEWMET$^{(R)}$ 25 were supplied to a fertilizer complex in Western Europe[4]. The units have been in operation for approximately five years and no significant corrosion problems have been found as of this date.

The selection of this alloy was based on plant corrosion test results, which are summarized in Table 3, along with results for modified Alloy 20 types, nominally Fe-20Cr-25Ni-5Mo-Cu.

In the early 1980's, Lewis began development work on an alloy material suitable for use in wet process acid produced from an ore with both high chlorine and fluorine contents. Agrico Chemical Co. was studying the possibility of producing acid from an ore deposit discovered in Sri Lanka at Eppawala. The ore had a number of unusual characteristics; chloride was present as part of the apatite crystal structure, at a level of approximately one percent, which cannot be removed by any physical processing step; varying amounts of highly oxidizing manganese minerals were present[5]. The high chlorine levels result in heavy corrosion for most metallic alloys. The presence of the manganese minerals causes an EMF of the acid ranging from 2.5 to 4 times that found in acid produced from more common ores.

LEWMET$^{(R)}$ 125, the end result of this development program, is a copper free alloy with an optimum balance of chromium and molybdenum to provide maximum general corrosion resistance and pitting resistance in acids having high levels of halogen contaminants. Laboratory corrosion test results on acid produced from Eppawala rock are shown in Table 4.

Plant corrosion testing of LEWMET$^{(R)}$ 125 by a western Canadian producer in 1990 revealed excellent corrosion resistance to acid produced from Togo rock. While actual corrosion rates were not measured, the original machining marks on the samples were still visible after test completion. Based on this test, one 500 MM elbow for an axial flow pump was put into service.

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TABLE 1

LABORATORY CORROSION TEST RESULTS
Acid Produced from Florida Ore

Test Conditions: Static Immersion
Unaerated
Temperature 90°C
Duration - 96 Hours

Corrosion Rate - MM/Y

% P_2O_5	316	Alloy 20	LEWMET$^{(R)}$ 15	LEWMET$^{(R)}$ 25
28	0.20	0.03	0.25	0.01
28 + 0.1% Cl-	0.51	0.11	-	0.04
54	0.20	0.10	0.36	0.05
54 + 0.1% Cl-	3.76	2.39	-	0.09

TABLE 2

CHEMICAL ANALYSIS AND MECHANICAL PROPERTY SUMMARY

WT. %	LEWMET$^{(R)}$ 15	LEWMET$^{(R)}$ 25	LEWMET$^{(R)}$ 125
Cr	28	28.5	23.5
Ni	8	BAL	BAL
Mo	2.2	4.5	7
Cu	3.2	3	-
Fe	BAL	16	16
Co	-	6	6
Mn	0.5	3	3
TENSILE (KG/cm^2) STRENGTH	7,700	4,900	5,800
YIELD (KG/cm^2) STRENGTH	5,600	2,700	2,800
% ELONGATION	18.0	55.0	55.0
% REDUCTION OF AREA	35.0	60.0	60.0
BRINELL HARDNESS	250	150	150

TABLE 3

PLANT CORROSION TEST RESULTS ACID PRODUCED FROM MORROCAN ORE

TEST LOCATION	CORROSION RATE - MM/Y	
	LEWMET$^{(R)}$ 25	Fe-20Cr-25Ni-5Mo
Reaction Vessel Slurry 28% P_2O_5 65/70°C	0.01	0.01/0.08
Filter Acid 28% P_2O_5 45/50°C	< 0.01	0.06/0.07
Product Acid 42% P_2O_5 45/50°C	0.02	0.19/0.18

TABLE 4

LABORATORY CORROSION TEST RESULTS

LEWMET$^{(R)}$ 125

Acid Produced from Eppawala Ore

Test Conditions: Static Immersion
Unaerated
Temperature 78°C
Duration - 700 Hours

% P_2O_5	Corrosion Rate - MM/Y
28, 1.17% F -, 0.6% Cl-	0.01
54, 1.17% F -, 0.6% Cl-	0.02

LEWIS Sulphuric Acid Pumps & Valves

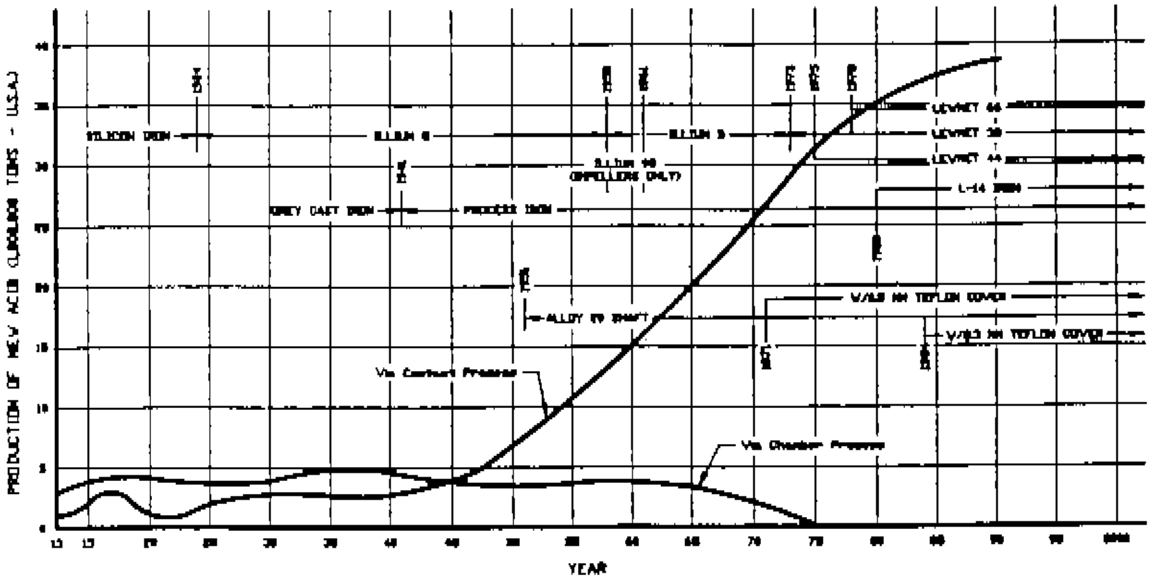


Figure 1. Chronological Development of Materials

ISOCORROSION CURVES FOR LEWMET ALLOY 55 IN SULPHURIC ACID

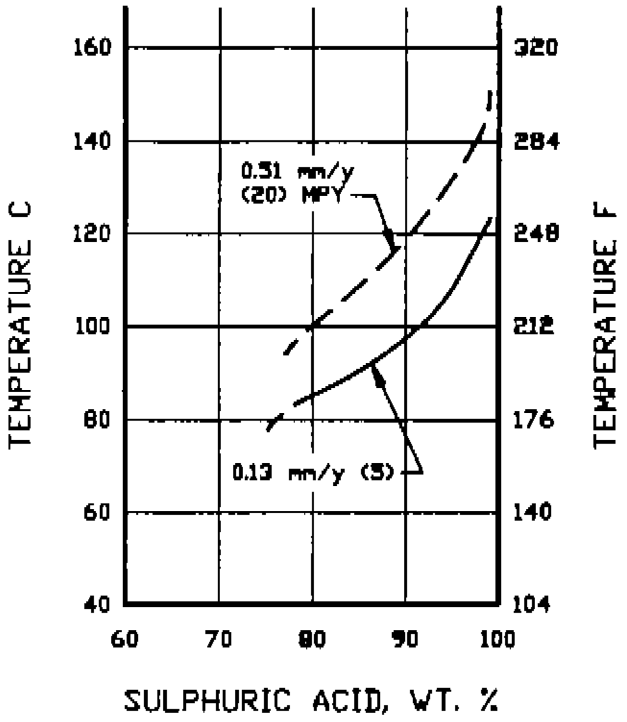


FIG. 2

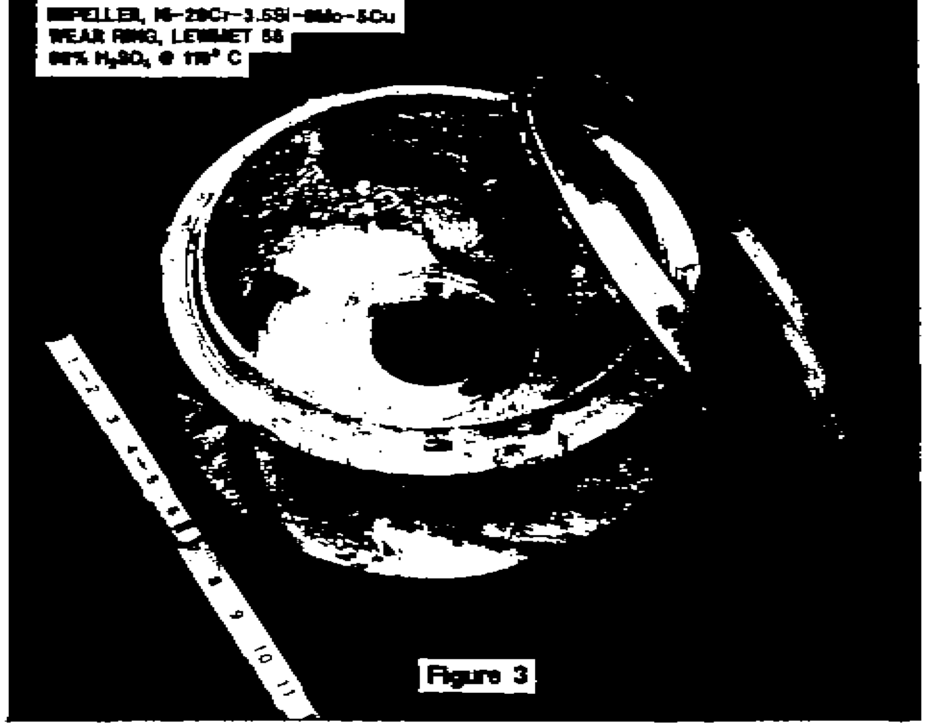
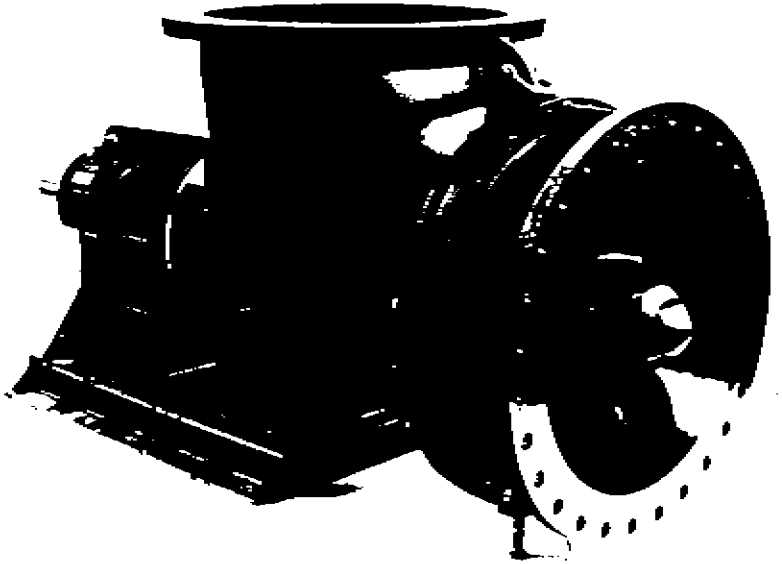


Figure 3

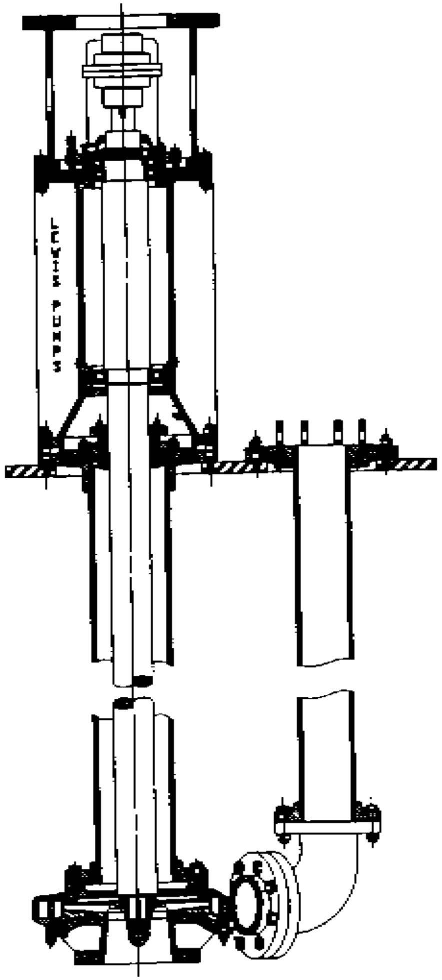
Figure 5



LEWIS 750MM AXIAL FLOW ELBOW PUMP

Figure 4

Cantilever-Shaft Pump for Phosphoric Acid Filtration and Dirty Sulphur Service



Note For sulphur applications, a steam jacket is added