ANNUAL TECHNICAL CONFERENCE OF CENTRAL FLORIDA SECTION OF
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS
MAY 25, 1996

DEVELOPMENT OF CORROSION RESISTANT WHITE IRONS FOR USE IN PHOS-ACID SERVICE

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ABSTRACT

Alloys with high corrosion and abrasion resistance are needed for many applications in mining and chemical processing and in particular in the phos-acid industry. In general, stainless steels have excellent corrosion toughness, but their abrasion resistance is marginal. On the other hand, most high alloy white irons have exceptional wear resistance but see corrosion problems in the above applications.

In this study, research has been carried out into the behavior of some new white iron alloys in a variety of corrosive and/or erosive conditions in comparison with some conventually applied stainless steel alloys. The different corrosion and/or wear mechanisms applied are discussed and the results of the tests are presented.

The experimental results indicate that chromium is a key element in the corrosion resistance of the white iron alloys and that the corrosion that occurred in these alloys is due mostly to the depletion of chromium at the boundaries between the carbides and the matrix and the attack that starts in this area. Some of the new test white iron alloys overcome this deficiency and show a corrosion resistance close to or even better than that of some stainless steels.

Because of their respectable corrosion resistance and their considerably higher wear resistance, the new alloy white irons have a much better combined overall corrosion-abrasion resistance than stainless steels such as CD-4MCu. Lab and field tests on specimens, test coupons and production pump components show that these new

special white irons have a combined corrosion-wear resistance of about five times better than ordinary CD-4MCu under typical severe corrosion and wear conditions, and appear to be promising candidates to replace the existing stainless steel materials now being used.

INTRODUCTION AND BACKGROUND

In the mining industry there is a need for metallic alloys to resist wear in a variety of applications. Examples here would be centrifugal slurry pump parts and pipe bends.

Industries such as coal, iron ore, copper tar sands, phosphate and even dredging employ large quantities of pumps, piping parts and other components manufactured in erosive resisting metallic alloys.

In a lot of these applications corrosion is considered a minor factor in relation to erosion. The alloys used in these cases are generally of the white iron type from the high chrome, chrome moly or high nickel (NiHard) families.

In certain industries such as in the phosphoric acid producing side of the phosphate industry, the chemical corrosion component is not insignificant in the cases above and the alloys noted above suffer significant corrosion damage eliminating them as practical materials for these services.

Stainless steel alloys such as the austenitic 316 type and Carpenter Alloy 20 (or even the high nickel irons such as Ni Resist[1-3]) type have excellent corrosion resistance but at Brinell hardnesses of 160-170 have very little resistance to erosion.

The phosphoric acid process involves the pumping of not insignificant quantities of coarse particle laden slurries in a corrosive media where the 316 and Alloy 20 give unsatisfactory service as a result of erosive losses.

The duplex stainless steel CD-4MCu with a Brinell hardness of 250 or so has good corrosion resistance and much better erosive wear capabilities than the austenitic stainless steels. CD-4MCu provides an improvement in overall performance over either the good corrosion resisting austenitic stainless steels or the high erosion resisting alloy white irons but still suffers heavily from erosive wear and falls short of what could be achieved by an alloy with the corrosive resistance of stainless steel and the erosive wear resistance of a white iron.

The high silicon irons with 12-18% Si are capable of resisting many acids at a high hardness of around 500 Brinell would seem to offer some possibilities. Unfortunately, their relatively low mechanical properties and poor producibility, particularly in larger sizes of components, limits their applications[1, 3-8].

Some austenitic, duplex, martensitic and austenitic-martensitic stainless steels are hardenable by an aging treatment at moderately elevated temperature. Through this process, the hardness and wear resistance can be increased considerably. For example, the hardness of a regular CD-4MCu grade is about 250HB, while a hardened CD-4MCu can have a hardness as high as 300HB or more. While the hardness is improved, the corrosion resistance of the stainless steel is usually reduced, to a large extent.

The theory behind the corrosion resistance of a metallic material is the formation of a passive oxidation layer/film. In order to form and maintain such a protective layer on a material surface under certain corrosive conditions, the material/alloy has to meet certain requirements, and especially the general chemistry and distribution of chemical elements in its microstructure. For iron-based alloys, chromium is the most important element in forming the passive film to ensure the corrosion resistance, while in the case of other alloys elements such as molybdenum and nickel promote the stability and reformation of the passive film. There is a minimum chromium content required for the passive film formation. In stainless steel, a weak passive film forms at a chromium level of about 10.5%. For a stable passive film, the chromium level of stainless steels has to be 17-30%[9, 10].

In the case of white iron alloys, the situation is more complicated due to the existence of both carbides and matrix. Higgins[11] suggested that, for excellent corrosion resistance, the chromium content in the matrix of a white iron should be at least 13% and the total chromium level in the alloy should be 30 percent or higher to obtain the optimum mechanical properties and corrosion characteristics. He assumed that the general principle of the corrosion behavior of high-chromium white cast irons was similar to that of stainless steels. Trypin[12] *et al.* studied the abrasion and corrosion characteristics of alloyed white irons. It was concluded in their research that increasing the chromium content from 12 to 30 percent improved the corrosion resistance by up to 50 times. It was also indicated that the corrosion rate increased considerably with the increasing carbon content in the white iron alloys.

Recently, Shoaee[13] studied the corrosion characteristics of alloyed white irons. In his research, potentiodynamic corrosion testing, x-ray diffraction and electron microprobe techniques were applied to examine the microstructure and corrosion behaviors of the alloyed white irons. He concluded that, for an effective improvement in corrosion resistance, the chromium content in the matrix of white irons has to be 21 percent or higher. This minimum chromium level in the matrix was considerably higher than that of 13 percent suggested by Higgins[11]. The effects of carbon, nickel and molybdenum on corrosion resistance of white irons were also discussed[13].

Very limited attention has been paid in the past to the corrosion mechanisms of white irons. Although the early studies pointed out a minimum chromium content in the matrix of white irons and led to the further improvement of corrosion resistance of this type of alloys, the corrosion mechanisms as well as the functions of some other chemical elements still remained unclear. More recent studies[14-15] indicated that even the white iron alloys which contained 25-35%Cr (13-21%Cr or higher in matrix) and had a ferritic or duplex matrix could not provide satisfactory corrosion resistance under many application conditions including some flue gas desulphurization (FGD) services. In general, as compared to stainless steels, the corrosion-abrasion resistant white iron alloys seen to date have an outstanding wear resistance, but their corrosion toughness is still unsatisfactory in many situations. On the other hand, the wear resistance of stainless steels including martensitic and hardened grades is still lower or much lower than that of alloyed white irons.

The object of the following research is to look at corrosion and erosion resistance of some common high corrosion resistant and high erosion resistant alloys in comparison with some new alloys as to their total combined erosion/corrosion resistance.

TEST CONDITIONS AND RESULTS

The particular alloys tested are shown in Table 1. It can be seen that this includes a good wearing white iron alloy. A couple of good corrosion resistant stainless steels, two types of duplex stainless steel and a few new high chrome white iron alloys aimed at achieving the high corrosion resistance while at the same time a high erosion resistance.

1. Corrosion Tests

Two types of lab tests were carried out in this study, corrosion tests and corrosion-abrasion/erosion combination tests. The type of corrosion only tests carried out in this study was of the exposure corrosion testing type shown in Figure 1. Here testing specimens with a dimension of 20x20x4 mm were placed on a holder into a testing solution within a reaction flask. All the components that contact corrosion solution within the tester are made of high-grade quartz glass to insure the chemical stability. The temperature of corrosion solution is controlled by the regulated heating mantle. An electric motor for the stirrer is mounted to the platform extended horizontally from the top of the stainless steel frame. The motor speed is adjustable in the range of 50-1500RPM. Sled-type sample holders were used in the tests. The contact between a specimen and the sled-type holder is "point-tough" featured so that the total contact area is minimized. In a typical exposure corrosion test, up to nine specimens can be tested in a testing solution for 120 hours at a temperature of 70^{0}C. Normally, the testing solution is aerated with natural or synthetic air during a test.

Table 1 Test Materials

Alloy	*Material Type*	*Tensile Strength (ksi)*	*Hardness (HBN)*	*Tested in**
AW-01	25%Cr martensitic white iron	90	650	ET
NCAW-01	Duplex super alloyed white iron containing vanadium	70	400	ET, CT
T90G	Super alloyed white iron with mostly ferritic matrix	60	450	ET, PT, CT, FT
SAW-02	Super alloyed white iron with ferritic-austenitic duplex matrix	70	430	ET, CT
CD-4MCu	Commercial type duplex stainless steel	100	250	ET, CT, FT
CD-4MCu (H)	Hardened CD-4MCu	120	305	ET, PT, CT, FT
SS-316	Austenitic stainless steel 316	80	170	ET, FT
SS-A20	Austenitic stainless steel Alloy 20	80	160	ET, FT

* ET - Exposure Corrosion Testing; PT - Potentiokinetic Corrosion Testing; CT - Combined Corrosion-Abrasion Testing; FT - Field Testing.

The major exposure corrosion test results are shown in Table 2 and Figures 2 through 4. Table 2a. lists the corrosion rate of six (6) test alloys under low pHs and high (NaCl) chlorides. The comparison of corrosion resistance among the test alloys at different pH and chloride levels is demonstrated in Figure 2. It can be seen that as the acidity and chloride level increased in the solutions, the corrosion rates of the test alloys increased rapidly during the tests. Among the test alloys, the duplex stainless steel CD-4MCu showed the best chemical stability in the above solutions. The corrosion resistance of regular 25%Cr alloyed white iron in the low pH and high-chloride environment was very limited. The super alloyed white irons with either mostly ferritic

Table 2a. Exposure Corrosion Test Results

ALLOY	*CORROSION RATE, mpy*		
	Testing Conditions		
	pH=5.0 (H_2SO_4); Cl^- = 40,000ppm (w/NaCl) T = 158°F (70°C); Aerated	pH=2.0 (w/ H_2SO_4); Cl^- = 70,000ppm (w/NaCl) T= 158°F (70°C); Aerated	pH=1.0 (w/ H_2SO_4); Cl^- =100,000ppm (w/NaCl) T= 158°F (70°C); Aerated
AW-01	12.81	58.94	-
NCAW-01	-	0.76	-
T90G	0.25	0.52	2.01
SAW-02	0.29	0.62	2.95
CD-4MCu	0.22	0.45	1.34
CD-4MCu (H)	0.31	0.98	6.97

Table2b. Exposure Corrosion Test Results (continued)

ALLOY	*CORROSION RATE, mpy*		
	Testing Conditions		
	30% P_2O_5 industrial solution with high impurity level. T= 160°F (71°C); Aerated	54% P_2O_5 industrial solution with high impurity level. T= 190°F (88°C); Aerated	10% citric acid water solution T= 158°F (70°C); Aerated
AW-01	2204.51	-	453.56
T90G	0.03	0.13	0.09
CD-4MCu	0.05	0.30	0.12
CD-4MCu (H)	0.17	2.83	0.27
SS-316L	0.14	1.77	-
SS-A20	0.08	0.51	-

(T90G) or duplex (NCAW-01 and SAW-02) matrix presented outstanding corrosion resistance during the tests. The corrosion resistance of the super alloyed white irons were very close to that of regular CD-4MCu, up to 2.47 times better than that of hardened version CD-4MCu, and much better (by up to over 100 times) than that of 25%Cr alloyed material (AW-01).

The results of the exposure corrosion tests in phosphoric and citric acid solutions are listed in Table 2b. Both the 30%P_2O_5 and 54%P_2O_5 industrial solutions contained high level of impurities such as SO_4 and fluorides, which made these industrial phosphoric solutions/slurries very corrosive. The regular high chromium white iron AW-01 basically had no resistance to the corrosion attack, and its corrosion rate in the 30%P_2O_5 solution at 160^{0}F was over 2200 mpy (see Figure 3). Surprisingly, super alloyed white iron T90G showed the best corrosion resistance which was 67% to 21 times better than those of the test stainless steels.

Figure 4 shows the comparison in corrosion resistance of some test alloys in 10%citric acid water solution at 158^{0}F (or 70^{0}C). Again, the T90G super alloyed white iron demonstrated the best corrosion resistance among the test materials. The corrosion resistance of T90G was 200% better than that of hardened version CD-4MCu and over 5000 times better than that of 25%Cr martensitic white iron (AW-01).

2. Combined Corrosion-Abrasion Tests

In many applications, both corrosion and abrasion occurs simultaneously and intensively. It is of great importance to evaluate both corrosion and abrasion resistance of materials in a combination test. Such a test can be realized by using corrosive slurry in a wear tester. In the present study, a Coriolis wear tester was used with sand slurry containing low pH and high chlorides.

The Coriolis Wear Tester[16,17] consists of a bowl with four removable arms/specimen holders that rotates around a vertical axis (see Figure 5). The stainless steel sample holders are lined with a wear resistant urethane mold, the cavity of which is T-shaped with a flow passage adjacent to the specimen. During a test, the slurry is pumped into the spinning bowl from a big slurry tank through the flow loop. The agitators on the two vertical shafts keep the solid particles suspended in the test slurry. The major hydraulic and testing parameters are measured and monitored by a computerized system.

In most cases, the wear on a test specimen within a wear tester is largely accelerated from the wear intensity that occurs the real application on the same material with the same slurry. This will considerably reduce the test duration. As compared to the wear acceleration, the corrosion factor basically remains unchanged. Therefore, in order to reasonably simulate the weight loss on a material by the combined corrosion-erosion attack in a real application, the corrosion factor should be compensated during a combination tests. In the present research, a pre-corrosion test cycle is applied before each Coriolis cycle during a combination test.

A corrosion-Coriolis combination test consisted of four corrosion and four Coriolis cycles. Each corrosion cycle lasted 45 hours which was followed by a 3-hour Coriolis wear cycle. The corrosion cycles were carried out within the exposure corrosion tester (described earlier in this paper) in the aerated solution of pH2 (w/ H_2SO_4,), 70,000ppm chlorides (w/NaCl) at 70^0C ($158F^0$). In the Coriolis wear cycles, the slurry was made of water and silica sand with size of 270 microns (D50). The test slurry had 1.10 S.G and the same pH and chloride level as selected in corrosion cycles, but at ambient temperature. The Coriolis Tester operated at 8 gal/min flow rate and 950 RPM bowl speed.

The results of combined corrosion-abrasion/erosion tests are listed in Table 4. In the corrosion cycles under pH2 and 70,000ppm chloride, both duplex stainless steels and super alloyed white irons showed excellent corrosion resistance. The ranking in corrosion rate of the alloys in the combination test was consistent with that obtained in the pure exposure corrosion tests which was described in the previous section of the paper.

In the combination tests, the super alloyed white irons showed combined corrosion-abrasion resistance much superior to that of the duplex stainless steels. Among the super alloyed white irons, T90G was the best, the combined corrosion-abrasion resistance of which was about 27% better than NCAW-01 (duplex super white iron containing vanadium) and 504% over regular CD-4MCu.

Table 4 Results of Combination Tests

Material/ Sample	**Corrosion Cycle***		**Coriolis Cycle****		**Combination Results*****	
	Weight loss, mg	corrosion rate, mpy	Weight loss, mg	Wear rate, micron/hr	Weight loss, mg	Corrosion portion,%
NCAW-01	12.43	0.58	631.3	8.47	643.8	1.93
T90G	9.4	0.43	496.1	6.66	505.5	1.86
SAW-02	10.8	0.50	505.6	6.79	516.4	2.09
CD-4MCu	8.0	0.37	3047.2	40.41	3055.2	0.26
CD-4MCu (H)	14.7	0.67	1208.9	16.03	1223.6	1.22

* The corrosion weight loss is the total weight loss occurred on a specimen during the four 45-hours' corrosion cycles of a combination test. And the corrosion rate is calculated based on the total/collect weight loss in a 180 hours' time period.

** The weight loss is the total weight loss of a specimen collected during the four individual 3-hours' Coriolis wear cycles of a combination test, and the wear rate is the average wear rate during the wear cycles.

*** The weight loss is the total weight loss during an entire combination test. The "corrosion portion" is the percentage of the corrosion weight loss over the total weight loss during a combination test.

During the combination tests, the total weight loss of the test alloys depended on their overall corrosion-abrasion resistance. The weight loss in the corrosion cycles on these alloys was only about 2% of their total weight loss in the entire combination test. This indicated that erosion/abrasion mostly controlled the weight loss of the tested highly corrosion resistant alloys (including super alloy white irons and stainless steels). The corrosion factors would, however, become much more significant and controlled on the weight loss of alloys with relatively low corrosion resistance during a combination tests[18]. At the same or similar level of hardness and pure wear resistance, the weight loss of test alloys with different corrosion resistance may vary five times or more due to the corrosion effects[18]. On the other hand, the alloys such as T90G, SAW-02, NCAW-01, CD-4MCu and CD-4MCu (H) which have about the same level of corrosion resistance may show a huge difference (up to 604% among the alloys) in weight loss during the test due to the difference in hardness or pure wear resistance. Figure 6 summarize the weight loss of the test alloys during the entire combination test.

3. Field Tests

Pump Components were tested in gypsum tailings service which operated in a phosphoric acid processing environment. The slurry consisted of phosphogypsum crystal solids very angular in shape, having a maximum particle size of 63 microns, and make up water. Make up water was provided from two different sources; one containing approximately 2.4% P_20_5, 0.5% $S0_4$, 1.1% fluorine and other impurities, and the other source containing clay/water mixture.

Figures 7 and 8 give a comparison in service life of pump impellers respectively made of T90G and CD-4MCu materials. Pump operating conditions for each was approximately the same. Both impellers were-installed in 8 inch discharge slurry pumps. The CD-4MCu impeller was a 26.5 inch diameter, and the T90G was a 24 inch diameter; therefore the T90G impeller operated at approximately 10% higher rotational speeds. After only about 3 months service, a brand new CD-4MCu impeller was badly worn out and had to be replaced with a new one.

Further inspections of the T90G impeller were made at 7 and 12 months. Measurements from all inspections were taken and are recorded in Figure 9. Measurements are compared to original wall thickness per design (not to that as cast) and in some cases the "as cast" thickness slightly exceeds theoretical manufacture design as normal casting tolerances allow. Although measurements are shown to three decimal places in Figure 9, they are not accurate to this level. At the 3 month inspection, wall thickness was gauged with transfer calipers, and measured with a tape measure. After this inspection it was realized that the wear rate was very low, therefore dial calipers were used for measurements at the 7 and 12 months inspection to provide more "resolution".

As seen in table Figures 9 and 10, the T90G impeller was still in good condition after one year service, wearing only approximately ¼", and very evenly. The T90G impeller is expected to give at least 2&1/2 to 3 years service, as compared to approximately three months for the CD-4MCu impeller.

CONCLUSION

Separate corrosion, corrosion/erosion and field tests have been carried out on some corrosion resistant stainless steels, or high wearing white irons and some new alloys to determine their performance under different separate and combined erosion corrosion conditions.

As expected, the stainless steels did very well in the pure corrosion conditions and the white irons did well in the largely erosive conditions.

The new alloys showed very respectable corrosion resisting capability and in the combined erosion and corrosion test did better than all others. These results were confirmed on practical tests in the field.

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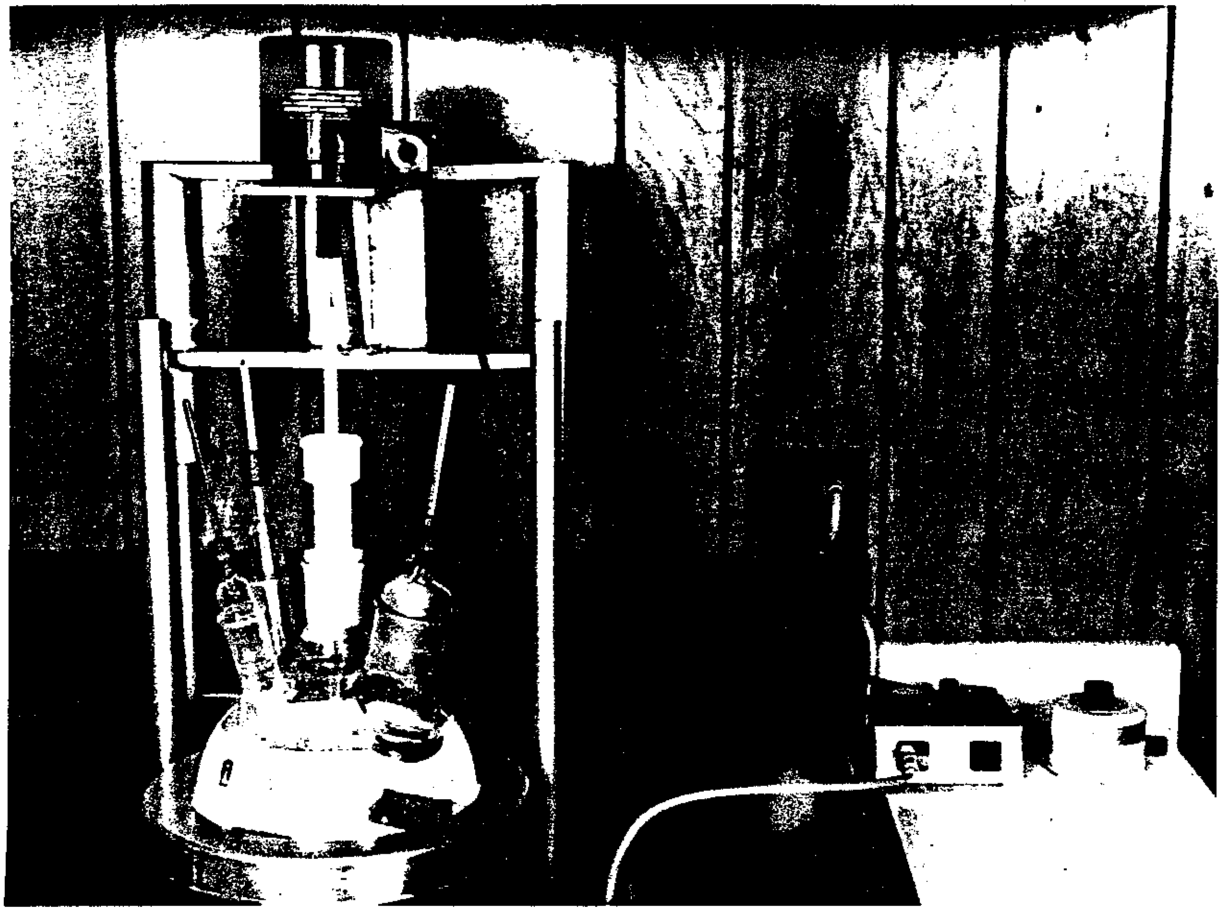


Figure 1 Exposure Corrosion Tester

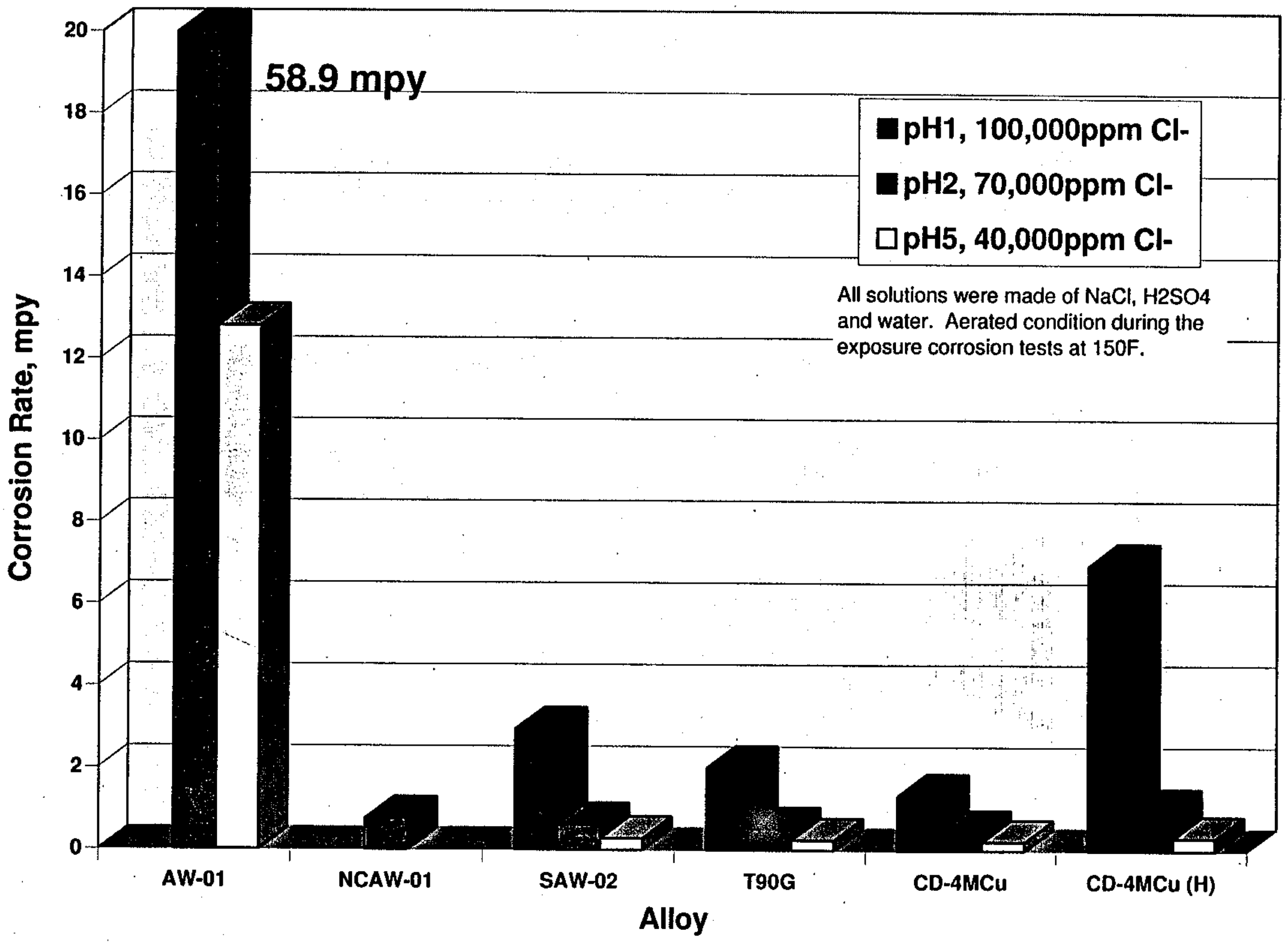
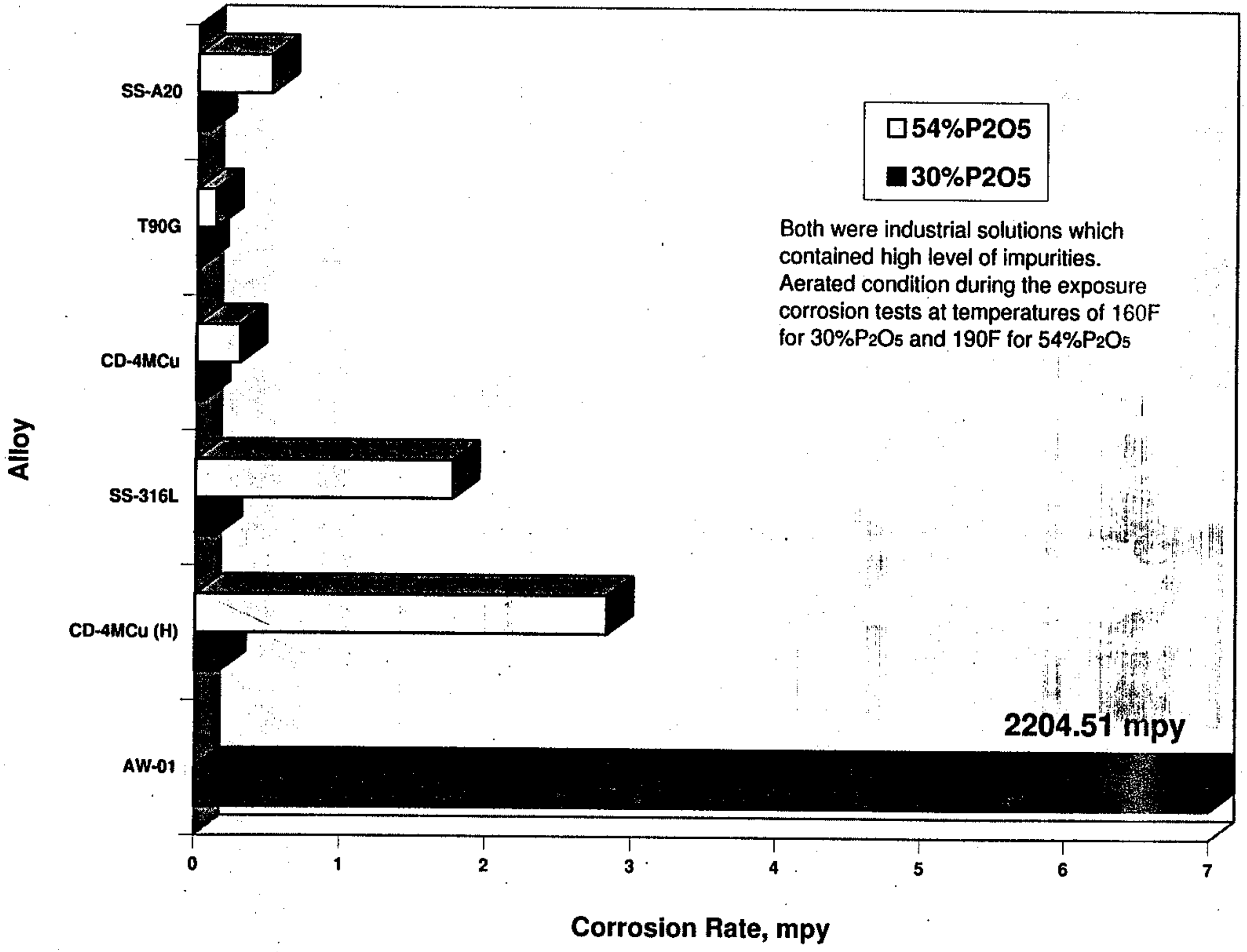


Figure 2 Showing Corrosion Resistance of Test Alloys under the above FGD Conditions



Both were industrial solutions which contained high level of impurities. Aerated condition during the exposure corrosion tests at temperatures of 160F for 30%P_2O_5 and 190F for 54%P_2O_5

Figure 3 Corrosion Rate of Test Alloys in Industrial Phosphoric Acid Solutions

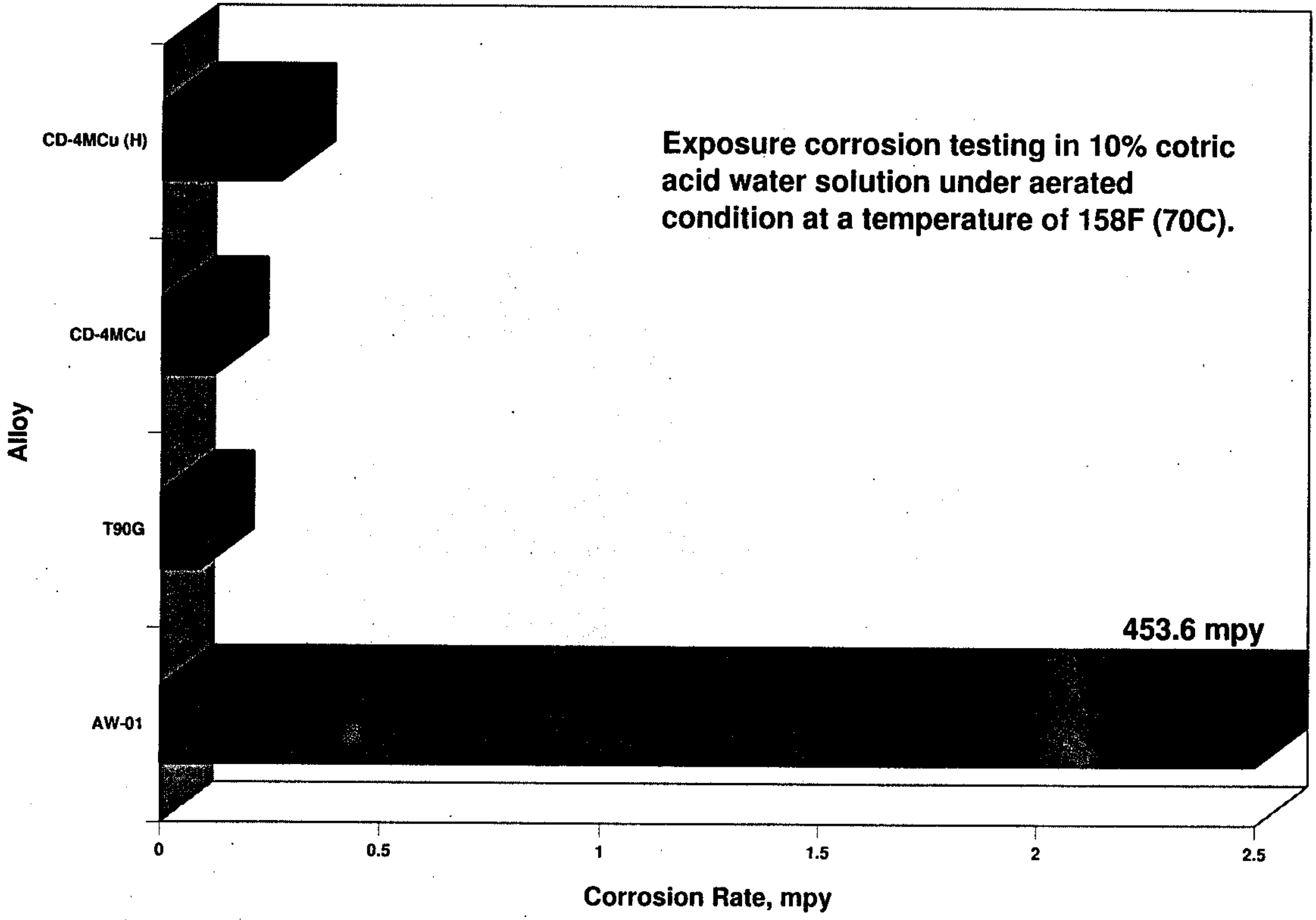


Figure 4 Showing Corrosion Resistance of Test Alloys in 10% Citric Water Solution.

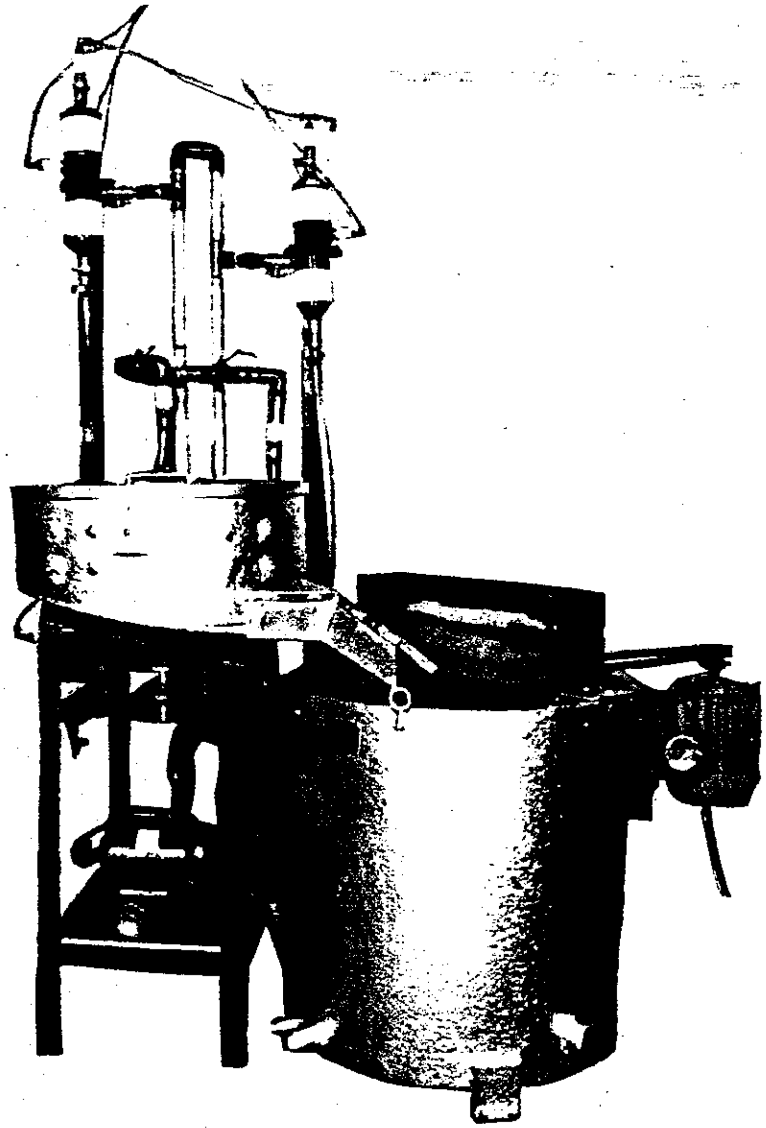


Figure 5a. Coriolis Wear Testing Machine

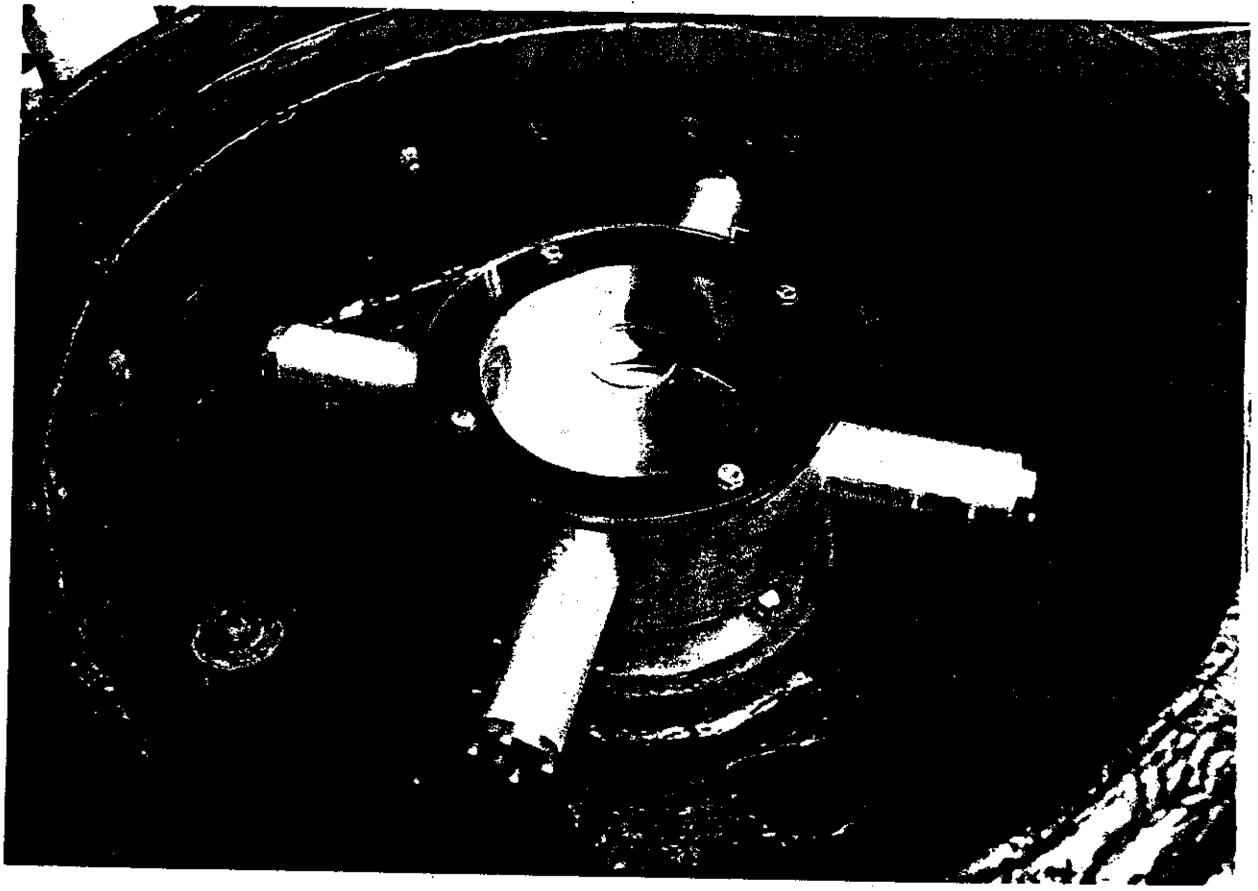
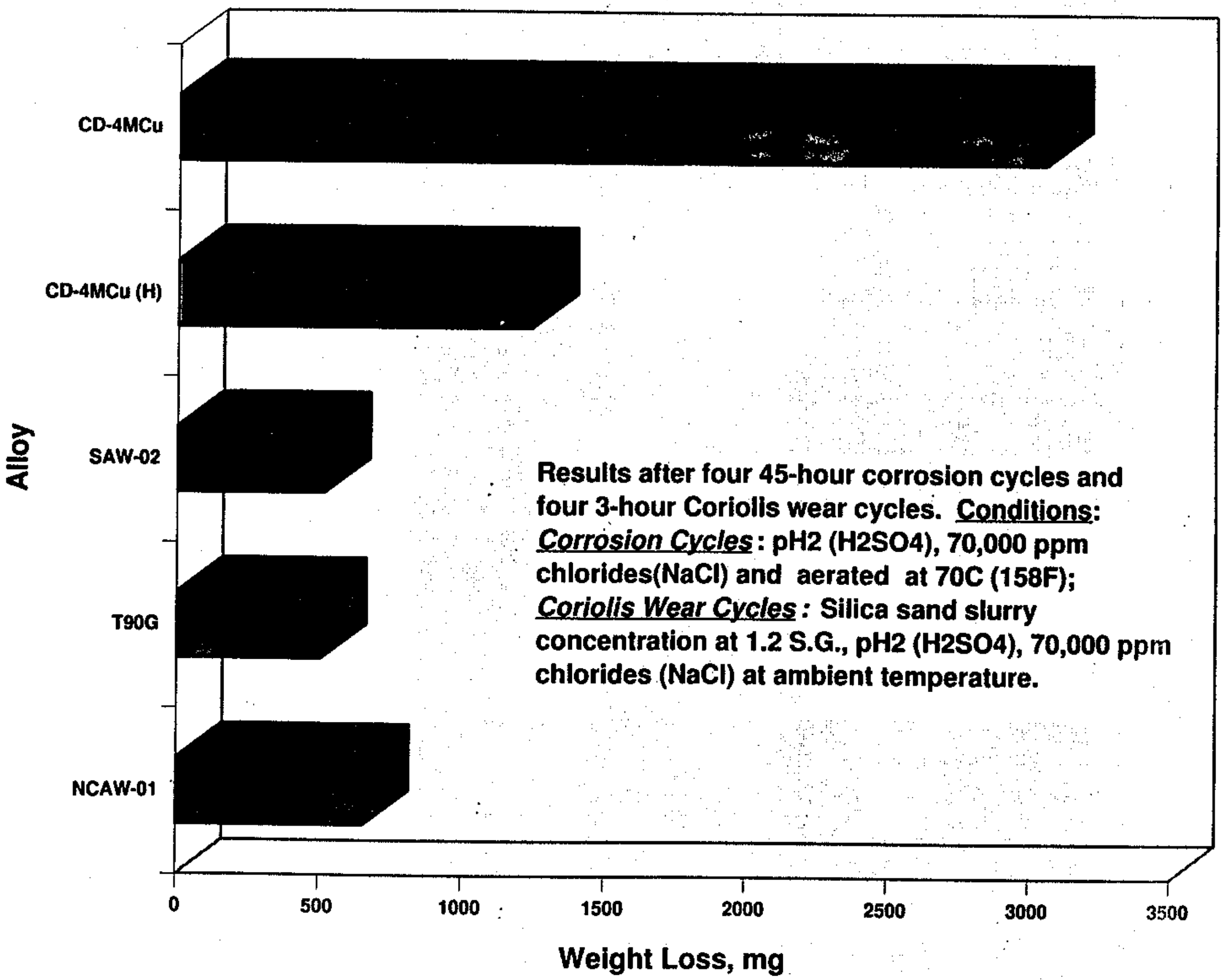


Figure 5b. Showing the Bowl of the Coriolis Wear Tester

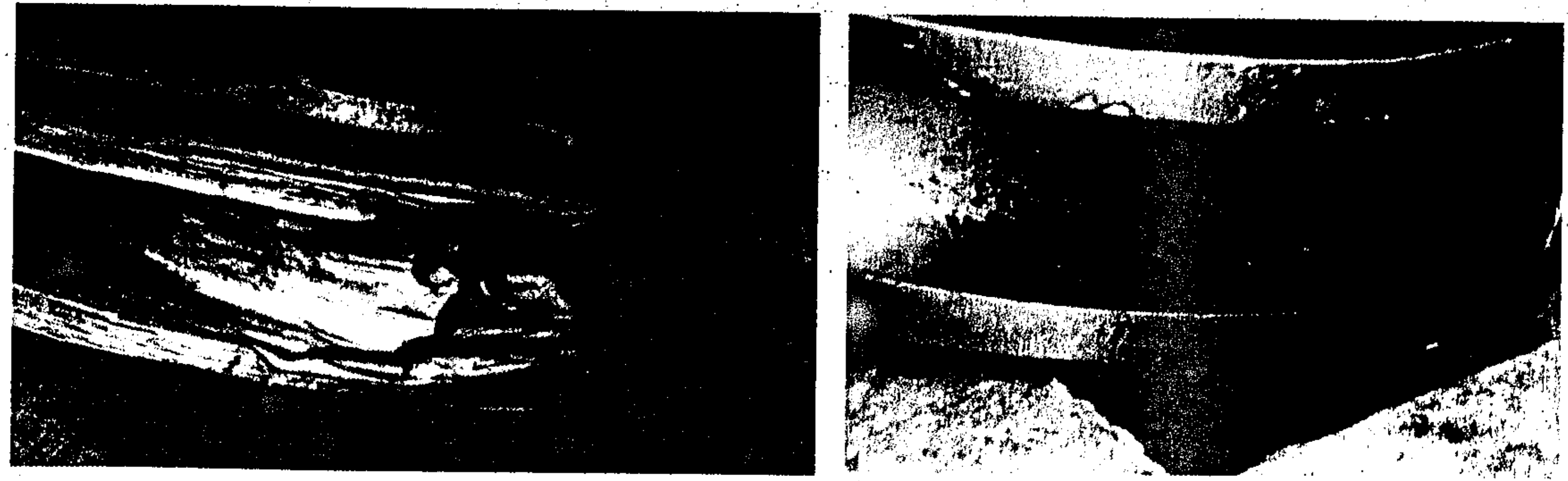


Results after four 45-hour corrosion cycles and four 3-hour Coriolis wear cycles. <u>Conditions</u>: *<u>Corrosion Cycles</u>* : pH2 (H2SO4), 70,000 ppm chlorides(NaCl) and aerated at 70C (158F); *<u>Coriolis Wear Cycles</u>* : Silica sand slurry concentration at 1.2 S.G., pH2 (H2SO4), 70,000 ppm chlorides (NaCl) at ambient temperature.

Figure 6 Weight Loss of the Tested Alloys during Combination Tests

(the weight losses in corrosion cycles are too small to see in above chart)

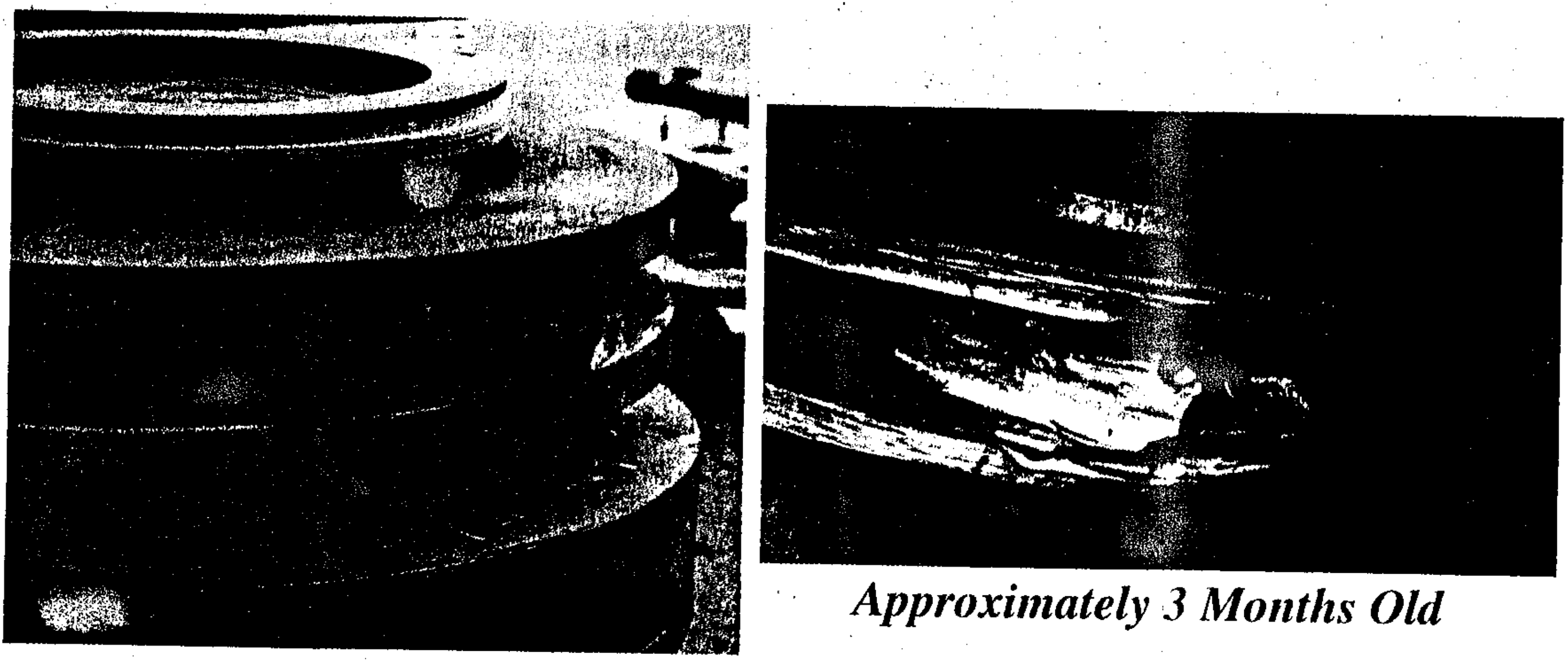
Fig. 8: Wear performance comparison of CD4MCU and Gasite® T90G impellers after 3 months of service.



CD4MCU Impeller

Gasite T90G Impeller

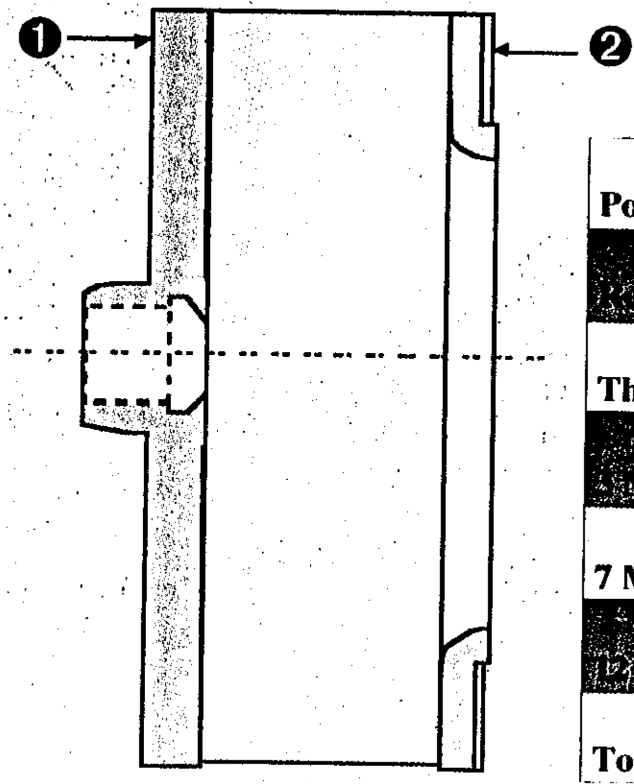
Fig. 7: A new and a worn-out CD4MCU impeller after 3 months of service.



New

Approximately 3 Months Old

Fig. 9: Thickness measurements on a Gasite® T90G Impeller.



Position	❶	❶	❷	❷	❷
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Theoretical New (in.)	≈1.575	≈1.575	≈1.457	≈1.457	≈1.457
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
7 Months (in.)	≈1.345	no reading	≈1.205	≈1.225	≈1.210
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Total Wear (in.)	≈.240	≈.219	≈.281	≈.191	≈.253

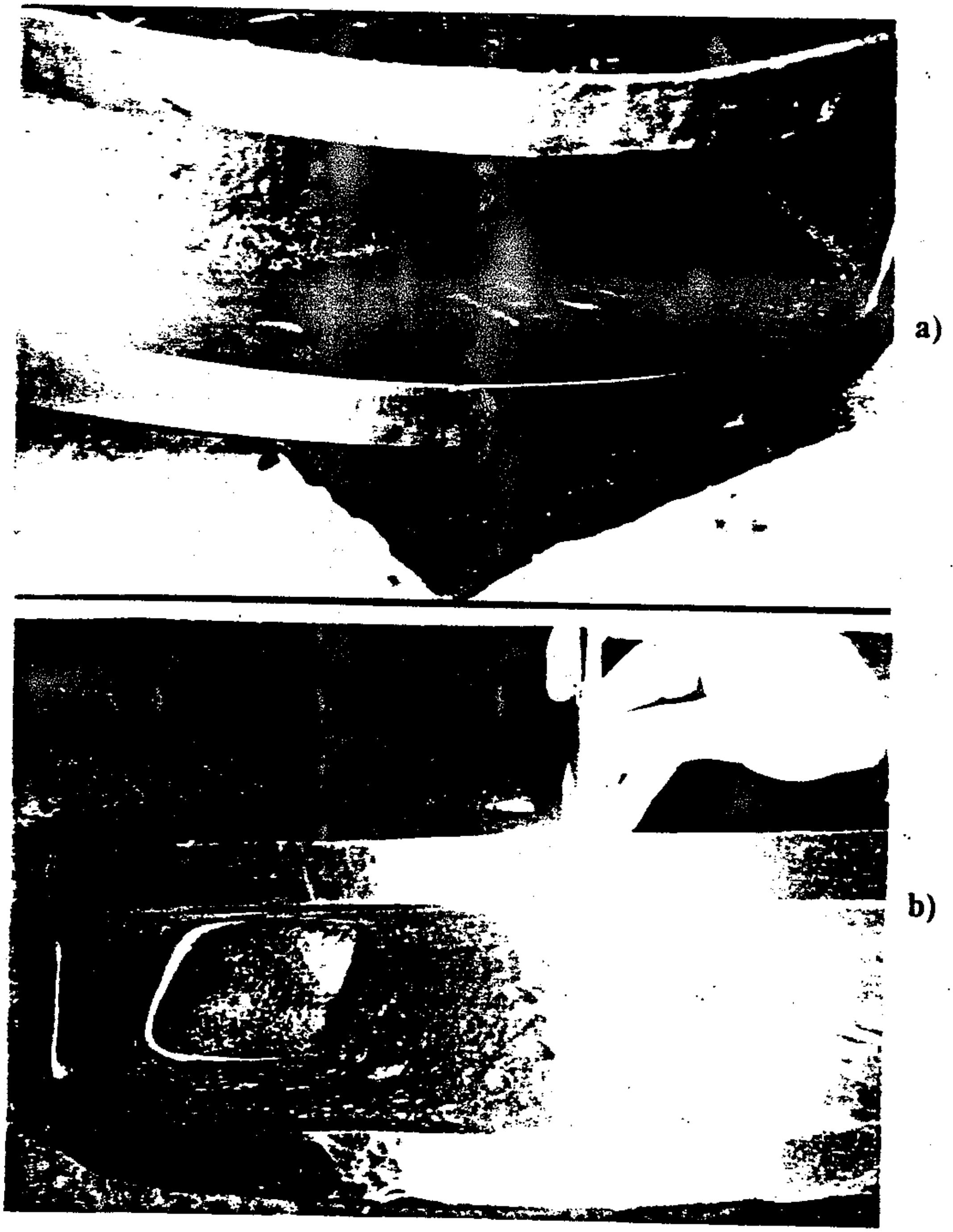


Figure 10 T90G Impellers in Phophoric Acid Service
a) Impeller after Three (3) Months' Service
b) Impeller after One Year Service