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HIGH-TEMPERATURE CORROSION IN GAS TURBINES AND STEAM BOILERS BY FUEL IMPURITIES.  
PART VIII. EVALUATION OF THE EFFECTS OF MANGANESE, CALCIUM, AND SEVERAL HEAVY  
METALS ON CORROSION AND SLAG FORMATION

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### INTRODUCTION

There are two recognized approaches to controlling vanadic corrosion. Both result in the production of dry, non-adhering and therefore non-corroding slags. The more widely accepted approach is the formation of higher melting compounds in the slag via fuel additives. The other approach utilizes low excess air operating conditions which produce higher melting, lower valence state vanadium compounds and less  $SO_3$  which reduces sulfate in the slag. In earlier studies presented in this series of papers<sup>1</sup>, we have examined magnesium, silicon, aluminum, and combinations of these elements as additives. Many elements have been tried as additives with varying degrees of success<sup>2-6</sup>. The difficulty in obtaining sufficient data to thoroughly evaluate an additive partially explains the paucity of information on combination systems. Our electrochemical approach to measuring corrosion rates coupled with the stepwise linear regression analysis of the data helps fill this gap and offers a rapid but thorough screening of an additive system. The technology in this area, particularly for gas turbines, has been toward use of lower quality fuels and higher temperatures for better efficiency. The result has been a demand for an additive with better sodium and temperature tolerances. In the last paper in this series<sup>1</sup>, we presented data on the magnesium-aluminum-silicon system which showed considerable promise in this area. In this paper, we are presenting data obtained on several other systems of interest.

Manganese improves combustion efficiency which permits lower excess air operation<sup>10</sup>. Available commercially are combinations with magnesium and/or silicon to permit low excess air operation where possible with the magnesium and/or silicon present to inhibit slagging and corrosion in the conventional manner. The purpose of the study on manganese was to find if it has any inhibiting effects in the conventional manner or interferes with magnesium and/or silicon. The purpose of studying calcium, zirconium and the rare earths was to evaluate their effects on the corrosion process and slag characteristics.

### EXPERIMENTAL

**Materials.** The melts were prepared from reagent grade chemicals obtained from Fisher Scientific Company with the exception of the following. The cerium oxide, zirconium oxide and rare earth oxide mixture were obtained from the Davison Chemical Division of W.R. Grace and Company. The rare earth oxide mixture contained approximately 48%  $CeO_2$ , 23%  $La_2O_3$ , 5%  $Pr_6O_{11}$ , 16%  $Nd_2O_3$ , 4%  $Sm_2O_3$  and 4% of other rare earth oxides. Samples of 40 g size were prepared by weighing appropriate quantities of the constituents and thoroughly mixing to insure a homogeneous sample.

The fuel for the burner test was reagent grade hexanes and xylenes. Vanadium was added in the form of an oil-soluble material, vanadium Ten-Cem<sup>TM</sup> (6 percent vanadium), obtained from Mooney Chemicals, Inc. The sodium was added as an oil-soluble sodium-naphthenate prepared in this laboratory by neutralizing an industrial grade naphthenic acid with sodium hydroxide. The final product contained 4.3 percent sodium as determined by atomic adsorption. The magnesium was added as KONTOL<sup>TM</sup> KI-15 containing 10 percent metal. The silica was added as KONTOL<sup>TM</sup> KI-39d, containing 16 percent metal. The magnesium-silicon mixture was KONTOL<sup>TM</sup> KI-18d containing 8 percent of each metal. These are oil-soluble compounds from the TRETOLITE DIVISION of PETROLITE CORPORATION. The aluminum source was a sulfonate obtained from Witco Chemicals Company containing 14.4 percent metal. Sulfur was added as a substituted 1, 2-dithio, 3-thione (36 percent sulfur)

prepared in the TRETOLITE DIVISION's pilot plant.

**Electrochemical Measurements.** The corrosion rate measurements were made in an electrochemical cell consisting of three electrodes immersed in a slag of the desired composition. The corrosion current was determined from polarization curves or by the polarization admittance technique. The cell, corrosion rate measuring apparatus, source of materials, and sample preparation techniques are described in our earlier paper<sup>7</sup>.

**Slag Test.** The slag test consisted of burning a fuel containing the desired levels of contaminants and inhibitors. The flame impinges upon a coupon which is adjusted to give the desired temperature. The slag characteristics are evaluated by measuring the amount of material that can be brushed from the coupon. The test is described in much greater detail in an earlier publication<sup>8</sup>.

## RESULTS

Corrosion rate data from  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5\text{-MnO}_2$  systems containing various combinations of magnesium and silicon are presented in Table I - III. The correlation equations generated by the technique described earlier<sup>9</sup> are presented in Table V. Comparisons of corrosion rates found in these slags with other additive systems at 800° and 900° are given in Figure 1 and 2. Data for the  $\text{Na}_2\text{SO}_4\text{-CaSO}_4\text{-V}_2\text{O}_5$  system are given in Table IV. The correlation equations for this system and those containing aluminum, silicon and lead are given in Table V. Also included in Table V are equations for the systems containing  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , and  $\text{ReO}_2$  the rare earth oxide combination. The data for these are not included to maintain a reasonable size for this paper. However, these data are available on request from the authors. The correlation equations for the  $\text{MgSO}_4$  and  $\text{MgSO}_4\text{-SiO}_2$  systems are included for comparison with the data presented in this paper. The plots for these two are also found in Figure 1 and 2. In all cases, the Na/V coefficients are positive indicating the strong corrosion promoting effect of sodium. The coefficient for Mn/V is positive indicating that manganese promotes corrosion. We examined several other cases where the Mn/V + Pb ratio was held at 2. In those cases, the Mg (+Si)/V (+Pb) ratios were negative indicating that the additive inhibited corrosion. We chose those cases because in actual practice, the manganese level is more likely to be held constant while the Mg + Si level varies with the trace metal content in the fuel.

Another interesting observation was that although calcium was an inhibitor when present alone, it promoted corrosion in relation to aluminum and silicon when all were included. Although the rare earths had negative coefficients, corrosion currents predicted by the correlation equations indicated that these materials were not inhibitors. All coefficients are included in the correlation equations although they are not always statistically significant. In those cases in which the F level was below approximately 2.25, there is less than a 95% chance that all the coefficients are significant for the correlation. However, addition of these does not materially effect the standard error and it is worthwhile to include these in our examination of their effect on the corrosion rate.

Slag friability data for the calcium-aluminum-silicon system compared with magnesium and magnesium-silicon are presented in Table VI. The data for various Na/V levels are summarized for comparison. There were not enough data to evaluate with the linear stepwise regression analysis technique. However, the effect of sodium, additive and temperature are clearly evident. At 820°, the Ca-Al-Si system compares favorably with the Mg-Si system. However, at 900° and particularly the high Na/V ratios, the friability decreases very rapidly.

## DISCUSSION

Over the past several years, the trade literature has abounded with claims for the effects of manganese on fireside corrosion, slag problems and cold-end corrosion<sup>10</sup>. There now appears little doubt that manganese as well as a few other metals such as iron and copper will reduce carbonaceous effluents or smoke through

more efficient combustion processes<sup>11</sup>. This type of additive is known as a combustion improver.

The minimum level of excess air required to eliminate smoke is a function of the engineering of the piece of equipment. Smoking can occur even in a gas turbine in spite of an overall oxygen/fuel ratio of 15 passing through the machine. The problem is caused by burner tip malfunctions and lack of available oxygen in the burner cans. Excess air is used to a lesser extent in other types of combustion equipment such as boilers to prevent smoking. During combustion of low quality fuels under excess air conditions, pentavalent vanadium compounds such as  $V_2O_5$  and  $NaV_2O_6$  with low melting points occur. Moreover, there is an increased production of  $SO_3$  which leads to formation of  $Na_2SO_4$  in slags and  $H_2SO_4$  downstream. A combustion improver allows operation near the stoichiometric ratio of air to fuel eliminating the problem delineated above. Furthermore, lower excess air operation yields considerable fuel savings due to more efficient operation of the burner.

Use of a combustion improver does require careful application by the operator. If the equipment does not permit good control of excess air, the air/fuel ratio, protection will not be attained in this manner. A combination additive has many benefits for equipment with poor control of air/fuel ratio. The manganese yields all the advantages of low excess air operation while magnesium and/or silicon gives protection during periods of excess air operation. A question we have tried to answer here is: Does manganese interfere with the corrosion inhibiting effects of magnesium and silicon?

The data in Table I reveals that manganese is not an inhibitor and appears to promote corrosion. We feel that this effect is due to addition of liquids to the melt by the manganese. The effect of manganese on the inhibiting effect of magnesium and magnesium-silicon are shown in Table II and III and Figure 1 and 2. Manganese detracts from the inhibiting effect of magnesium and silicon, although satisfactory protection can be attained at 800° with the Mg-Si combination. Comparison of the Mn-Mg and Mn-Mg-Si curves with the Mg and Mg-Si curves in Figures 1 and 2 illustrate this point.

We know of no published work to corroborate these findings and would welcome experiments of this nature. However, the laboratory data presented here leads us to conclude that manganese in combination with magnesium and magnesium-silicon can be beneficial at lower temperature. At higher temperatures, manganese apparently contributes to the liquidus phase of the slag and can be detrimental to Mg and Mg-Si. In either case, the operator should apply Mn-Mg and Mn-Mg-Si combinations with a great deal of care and with full knowledge of the protection mechanism for this type of additive.

Calcium has been cited as a problem contaminant in fuels for gas turbines and boilers<sup>2</sup>. We evaluated calcium and several combinations with aluminum, silicon and lead. The conclusion is that calcium is a corrosion inhibitor and in the presence of aluminum and silicon exhibits a tolerance to sodium at 900° which is similar to that found for the Mg-Al-Si combination. However, a study of the slag data presented in Table VI indicates that calcium produces unacceptable slags, particularly at the higher temperatures and sodium levels. The adverse slagging behavior cancels benefits from corrosion protection. These results are consistent with private communications we have received from equipment manufacturers.

In our search for better vanadic corrosion inhibitors, we have evaluated several heavy elements. Data on zirconium, cerium and the rare earth mixture described above are presented in Table V. All of these systems exhibit corrosion rates similar to those for manganese and do not inhibit corrosion.

## CONCLUSIONS

1. Manganese contributes to corrosion in  $Na_2SO_4$ - $V_2O_5$  melts and will not inhibit corrosion by forming higher melting compounds.
2. Manganese interferes with the corrosion inhibiting effects of magnesium and silicon.

3. Combinations of manganese, magnesium and silicon are probably safe at 800°C (1473°F) or lower but not at higher temperatures such as 850° or 950°. The Mn-Mg-Si system is preferable to the Mn-Mg system.

4. Calcium inhibits  $\text{Na}_2\text{SO}_4$ - $\text{V}_2\text{O}_5$  corrosion and the calcium-aluminum-silicon combination has good sodium tolerance.

5. Calcium systems form tenacious slags that detract from their corrosion inhibiting effectiveness.

Measurements on the rare earth oxide mixture, on zirconium, and on cerium did not indicate any corrosion inhibiting properties for these systems.

#### REFERENCES

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TABLE 1

CORROSION RATES OF  $\text{Na}_2\text{SO}_4 - \text{MnO}_2 - \text{V}_2\text{O}_5$  SLAGS

WEIGHT RATIOS		CORROSION CURRENTS ( $\text{Ma}/\text{Cm}^2$ )					
$\text{Na}/\text{V}$	$\text{Mn}/\text{V}$	700°	750°	800°	850°	900°	950°
1	1	.0832	.1830	.3171	.8423	1.148	1.231
1	2	6.83	10.25	12.30	13.21	12.52	13.43
1	3	10.62	13.31	15.87	17.92	19.97	25.34
1	4	9.20	11.96	14.73	19.10	20.13	23.01
1	5	10.65	14.20	32.67	35.51	41.19	42.61
.1	1	7.63	8.51	10.39	13.26	17.91	23.87
.1	2	1.33	1.74	2.22	2.54	2.78	3.33
.1	3	.578	.650	.795	1.04	1.56	1.99
.1	4	10.69	10.36	10.16	12.03	15.37	16.04
.1	5	3.21	4.49	6.89	11.54	14.43	12.83
.01	1	6.21	18.63	27.94	27.94	27.94	31.04
.01	2	.742	1.15	1.35	1.64	2.18	2.52
.01	3	13.65	17.07	20.48	23.55	27.31	35.16
.01	4	1.21	1.60	1.46	1.75	3.54	4.51
.01	5	1.26	.762	.949	1.40	1.79	2.26

TABLE II

CORROSION RATES OF  $\text{Na}_2\text{SO}_4 - \text{MnO}_2 - \text{MgSO}_4 - \text{V}_2\text{O}_5$  SLAGS

WEIGHT RATIOS			CORROSION CURRENTS ( $\text{Ma}/\text{Cm}^2$ )					
$\text{Na}/\text{V}$	$\text{Mn}/\text{V}$	$\text{Mg}/\text{V}$	700°	750°	800°	850°	900°	950°
1	1	1	1.29	1.43	.644	.644	1.13	1.22
1	2	2	.284	.613	.643	.747	.852	.942
1	3	3	1.17	1.79	1.79	2.48	2.48	2.76
1	4	4	.016	.040	.051	.800	1.634	1.96
1	5	5	.017	.030	.642	.984	1.436	1.64
.1	1	1	.031	.053	.411	.455	.632	2.13
.1	2	2	.0188	.0286	.134	.406	.436	1.16
.1	3	3	.0015	.0031	.0031	.100	.137	.216
.1	4	4	.0015	.0015	.019	.026	.034	.059
.1	5	5	.0015	.0045	.019	.029	.035	.106
.01	1	1	.124	.350	.617	1.07	1.52	3.77
.01	2	2	.059	.096	1.11	1.32	2.18	1.65
.01	3	3	0	0	.0055	.0055	.011	.022
.01	4	4	.005	.011	.025	.028	.029	.029
.01	5	5	.122	.183	.305	.427	.589	.792

TABLE III

CORROSION RATES OF  $\text{Na}_2\text{SO}_4 - \text{MnO}_2 - \text{MgSO}_4 - \text{SiO}_2 - \text{V}_2\text{O}_5$  SLAGS

WEIGHT RATIOS				CORROSION CURRENTS ( $\text{Ma}/\text{Cm}^2$ )					
$\text{Na}/\text{V}$	$\text{Mn}/\text{V}$	$\text{Mg}/\text{V}$	$\text{Si}/\text{V}$	700°	750°	800°	850°	900°	950°
1	2	1	1	.09785	.2039	.2854	.4077	.5912	.8766
1	2	2	2	.0245	.1116	.2232	.3794	.4909	.6472
1	2	3	3	.0033	.0083	.2499	.3500	.4833	.6333
1	2	4	4	.0017	.0033	.1081	.1829	.3326	.4823
1	2	5	5	.0011	.0031	.0105	.1600	.2526	.4632
.1	2	1	1	.0037	.0075	.0125	.0131	.0225	.0299
.1	2	2	2	.0008	.0008	.0015	.0015	.00225	.0090
.1	2	3	3	.0009	.0013	.0019	.0019	.0019	.0085
.1	2	4	4	.0009	.0009	.0009	.0010	.0019	.0058
.1	2	5	5	.0023	.0023	.0034	.0046	.0068	.0091
.01	2	1	1	.0023	.0023	.0045	.0124	.0360	.0450
.01	2	2	2	.0011	.0044	.0111	.0313	.0469	.0603
.01	2	3	3	.0011	.0018	.0022	.0022	.0022	.0054
.01	2	4	4	.0023	.0023	.0034	.0034	.0045	.0068
.01	2	5	5	.0016	.0016	.0016	.0016	.0062	.0094

TABLE IV

CORROSION RATES OF  $\text{Na}_2\text{SO}_4 - \text{CaSO}_4 - \text{V}_2\text{O}_5$  SLAGS

WEIGHT RATIO		CORROSION CURRENTS ( $\text{Ma}/\text{Cm}^2$ )			
$\text{Na}/\text{V}$	$\text{Ca}/\text{V}$	800°	850°	900°	950°
1	1	65	108	81.2	54.2
1	2	17.1	34.1	47.8	54.5
1	3	18.7	33.4	28.0	32.7
1	4	3.73	6.35	9.69	11.2
1	5	6.59	7.33	14.6	32.3
.1	1	7.54	11.9	13.7	13.0
.1	2	3.31	4.26	4.72	5.67
.1	3	1.18	1.38	1.54	1.63
.1	4	.888	1.05	1.37	1.69
.1	5	.994	1.19	1.49	1.49
.01	1	19.9	24.4	28.1	23.7
.01	2	3.12	3.12	3.45	3.45
.01	3	2.43	3.21	4.86	6.61
.01	4	.044	.072	.092	.100
.01	5	.143	.428	.443	.457
.001	1	6.04	9.06	9.66	9.66
.001	2	2.01	2.29	2.73	3.01
.001	3	.290	.347	.463	.578
.001	4	.0966	.0966	.104	.112
.001	5	.214	.268	.322	.375

TABLE V

Correlation coefficients for the corrosion rate data

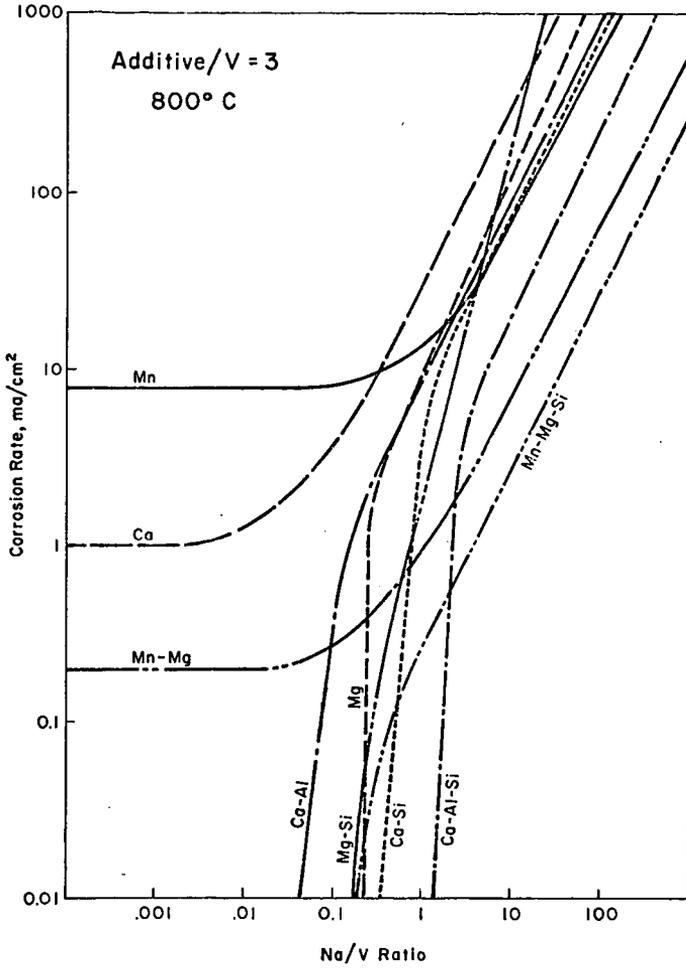
$$I_{corr} = A + B (Na/V) + C (Mg/V) + D (Mn/V) + E (Mo/V) + G (\text{Temp} \cdot C)$$

System	Correlation Equations						N Sets Data	F Level	No/V Range		Add/V Range		Temp. Range	
	A	B	C	D	E	G			Low	High	Low	High	Low	High
$Na_2SO_4-MgSO_4-V_2O_5$	-12.83	11.41	-	-1.894	-	0.0212	60	3.11	0.01	1.0	1.0	1.0	1.0	
$Na_2SO_4-MgSO_4-SiO_2-V_2O_5$	-11.66	19.61	-	-1.886	-0.6678	0.0187	137	0.89	0.001	1.0	2.0	6.0	700 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-MnO_2-V_2O_5$	-27.4	6.14	0.677	-	0.0414	0.0414	90	0.89	0.01	1.0	1.0	5.0	700 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-MnO_2-MgSO_4-V_2O_5, Mn/V = Mo/V$	-2.30	0.743	-0.184	-	-	0.0038	90	17.0	0.01	1.0	1.0	5.0	700 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-MnO_2-MgSO_4-SiO_2-V_2O_5, Mg/V=Si/V, Mn/V=Z$	-0.630	0.274	-0.024	-	-	0.0068	90	8.32	0.01	1.0	1.0	5.0	700 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-MnO_2-MgSO_4-PbO-V_2O_5, Mg/Pb+V=Z, Pb=V, Mn/V=Z$	-2.41	0.970	-0.232	-	-	0.0039	90	28.9	0.01	1.0	1.0	5.0	700 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-MnO_2-MgSO_4-SiO_2-PbO-V_2O_5, Mn/Pb+V=Z, Pb=V, Mg=Si$	-1.28	0.573	0.018	-	-	0.0016	90	0.89	0.01	1.0	1.0	5.0	700 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeSO_4-V_2O_5$	-3.89	29.9	-6.19	-	Si/V	0.0293	80	1.49	0.001	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeSO_4-Al_2O_3-V_2O_5$	-14.2	9.00	-1.76	-3.13	-	0.0262	106	3.16	0.01	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeSO_4-SiO_2-V_2O_5$	-9.65	7.15	-1.31	-	-2.11	0.0202	127	9.53	0.001	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeSO_4-Al_2O_3-SiO_2-V_2O_5$	-2.75	2.25	0.300	-1.08	-1.39	0.0068	96	0.71	0.01	1.0	3.0	6.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeSO_4-Al_2O_3-PbO$	-9.24	0.151	0.0081	-	-	0.0114	48	0.003	0.01	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeSO_4-Al_2O_3-PbSO_4$	-1.65	0.007	-0.117	-0.117	-	0.0026	44	0.294	0.01	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-ZrO_2-V_2O_5$	-13.9	3.70	-187	-	-	0.0190	64	0.670	0.001	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-CeO_2-V_2O_5$	-5.66	6.85	-1.67	-	-	0.0136	80	4.31	0.001	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>
$Na_2SO_4-ReO_2-V_2O_5$	-5.32	2.39	-5.62	-	-	0.0314	76	1.20	0.001	1.0	1.0	5.0	800 <sup>o</sup>	950 <sup>o</sup>

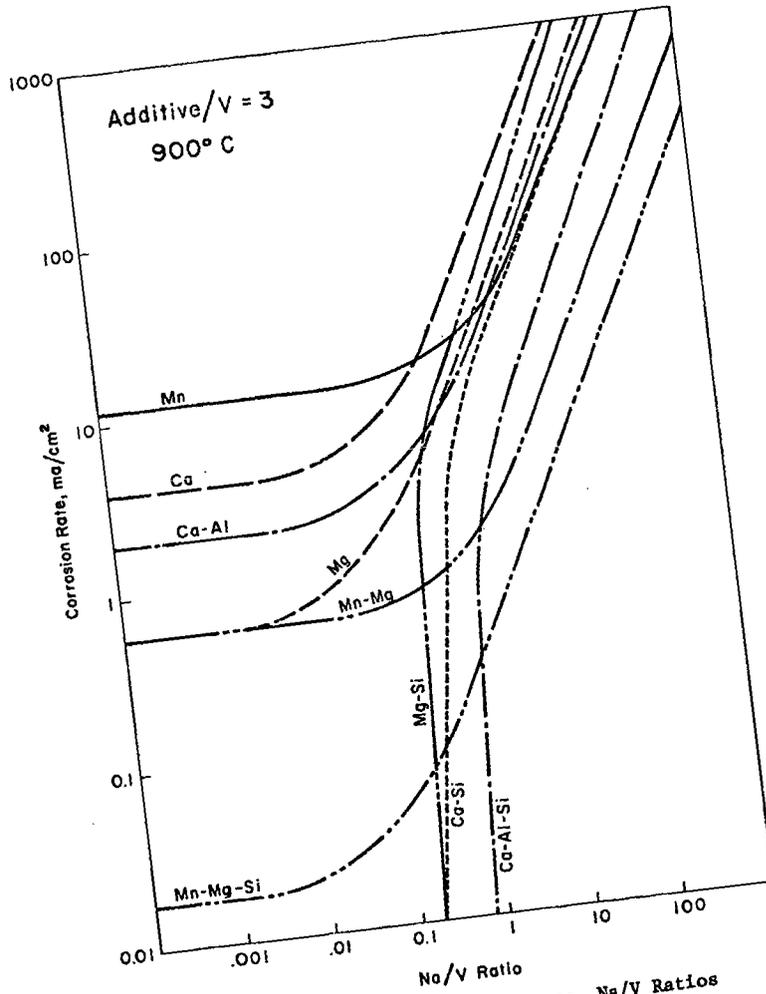
TABLE VI

Comparison of slag Test Data From the Calcium-Aluminum System  
With Data From the Magnesium-Silicon System

System	Average % Loss on Brushing	
	820°	900°
Na/V = 0		
Mg/V = 3	1.9	10
Mg/V = 6	11.7	20
Mg/V = Si/V = 3	58	59
Ca/V = .75, Al/V = 2.25, Si/V = 3	63	26
Na/V = .01		
Mg/V = 3	2.7	8.33
Mg/V = 6	35	14
Mg/V = Si/V = 3	53	6.3
Ca/V = .75, Al/V = 2.25, Si/V = 3	59	8.41
Na/V = .1		
Mg/V = 3	2.1	0
Mg/V = 6	22	13.2
Mg/V = Si/V = 3	35	18
Ca/V = .75, Al/V = 2.25, Si/V = 3	61	7.7
Na/V = 1		
Mg/V = 3	1.5	0
Mg/V = 6	4	3.3
Mg/V = Si/V = 3	11.2	15.3
Ca/V = .75, Al/V = 2.25, Si/V = 3	1.3	1.4



**FIGURE 1** - Corrosion Rates vs. Na/V Ratios for Several Additives at 800°C



**FIGURE 2** - Corrosion Rates vs. Na/V Ratios  
 for Several Additives at 900°C