

CORROSION BY MOLTEN MIXTURES OF SODIUM CARBONATE
AND VANADIUM PENTOXIDE

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I. INTRODUCTION

Corrosion costs American industry six billion dollars per year. New processes, higher temperatures, and higher pressures are daily making control of this corrosion more difficult. The unavailability of materials which resist corrosion at high temperatures has greatly retarded the development of more advanced steam generating equipment, gas turbines, rocket engines, and high temperature processing equipment in general.

The metal surfaces of the combustion chambers of boilers, gas turbines, and rocket engines sometimes become coated with slag. This slag, which is composed primarily of metal compounds, greatly influences the rate of corrosion at high temperature of the metal surfaces to which they adhere. To alleviate this problem either the slag forming agents must be removed from the fuels or materials of construction which resist corrosion at high temperatures in the presence of these slags must be developed.

Heavy fuel oils are one of the most important sources of energy presently being used for steam

generation and industrial gas turbines. Most of this fuel now being produced contains varying amounts of several different metals. The slag from these fuels, particularly those containing large amounts of sodium and vanadium, have proven to be extremely corrosive at temperatures of 650 °C and higher. Although extensive research work is being done on the removal of slag forming agents from heavy fuels, no satisfactory process has been developed. To combat this corrosion, possibly by the development of new alloys or through the use of inhibitors, a knowledge of the nature of the corrosive attack is necessary.

The purpose of this investigation was to study the corrosion of 1020 carbon steel, stainless steel 347, Hastelloy X, and Hastelloy B at temperatures between 650 °C and 980 °C in the presence of a mixture of sodium carbonate and vanadium pentoxide, and to attempt to establish the corrosion reactions which take place at these conditions.

II. LITERATURE REVIEW

The following section contains a literature review made in preparation for this investigation on the corrosion of steel at high temperature in the presence of a mixture of sodium carbonate and vanadium pentoxide.

Background

Heavy fuel oils represent a major source of energy for steam generation and gas turbines. The slag formed during the combustion of this fuel deposits on metal surfaces and at temperatures above 1100 to 1200 °F can cause rapid corrosion. This corrosion has hindered the development of more efficient, high temperature, heavy oil fueled boilers and has limited the use of these fuels in gas turbines.

This rapid corrosion is attributed to the presence of vanadium, sodium, and sulfur in the fuel⁽²⁸⁾. Different investigators have attributed the corrosion to either sodium sulphate, vanadium pentoxide, or a combination of these two components^(10,43). Others^(9,14) have obtained

data which indicate that one or more of the numerous sodium vanadate compounds are the corrosive materials.

Heavy Fuel Oil Ash

The ash content of even the heaviest residual fuel oil usually does not exceed 0.1 per cent. Although, under unusual conditions, one or two per cent ash may be found.

Since residual or heavy fuel oil is a residue of the process of refining crude oil, the ash-forming constituents originally present in the crude are concentrated. More advanced refining techniques make it possible to remove a larger portion of the crude for conversion into higher priced products, resulting in a residual fuel with higher ash concentration.

Origin of Ash Constituents. As with coal, some of the ash-forming constituents in the original crude had their origin in the organic materials from which the oil was formed. The balance is extraneous material resulting from contact of the crude with rock structures and salt brines, or picked up during production, storage, and transportation.

The chief sources of ash constituents in residual fuel oil are:

- (1) Oil soluble compounds indigenous to the crude oil.
- (2) Water soluble compounds in solution in water associated with the crude oil. These are usually salt solutions emulsified in the oil. Distillation breaks the emulsion and the inorganic salts remain in the residual oil fraction.
- (3) Various contamination products such as scale from pipes, tanks, and other equipment, salt water, refining catalysts, and corrosion inhibitors.
- (4) Corrosion products resulting from the reaction of acidic materials in the crude with metallic surfaces.

The analysis of ash of crude oil from various fields is shown in Table I. Table II shows nickel and vanadium content of South America crudes⁽⁴¹⁾. It should be noted that:

- (1) The percentage of each component varies widely in oils from different areas.

TABLE I
Analysis of Ash from Crude Oils

	California	Mid-Continent	Texas	Pennsylvania	Kansas	Iran	Iran
	Per Cent by Weight						
SiO ₂	38.8	31.7	1.6	0.8	10.0	52.8	12.1
Fe ₂ O ₃)	17.3	31.8	8.9	97.5	19.1	13.1	18.1
Al ₂ O ₃)							
TiO ₂)							
CaO	8.7	12.6	5.3	0.7	4.8	6.1	12.7
MgO	1.8	4.2	2.5	0.2	1.3	9.1	0.2
MnO	0.3	0.4	0.3	0.2	Trace	Trace	Trace
V ₂ O ₅	5.1	Trace	1.4	--	0.4	14.0	38.5
NiO	4.4	0.5	1.5	--	0.6	1.4	10.7
Na ₂ O	9.5	6.9	30.8	0.1	23.6	--	--
K ₂ O	--	--	1.0	--	0.9	--	--
SO ₃	15.0	10.8	42.1	0.9	36.4	2.6	7.0
Chloride	--	--	4.6	--	0.1	--	--

Thomas, W. H.: Inorganic Constituents of Petroleum, "Science of Petroleum,"
Volume II, p. 1055. Oxford University Press, London, 1938.

TABLE II
Vanadium and Nickel Content of
South American Petroleum

Location	Vanadium Concentration, ppm	Nickel
Bachaquero Heavy	390.0	45.0
Bachaquero	370.0	46.0
Bachaquero Light	49.0	5.5
Barinas	165.0	43.0
Boscan	1400.0	100.0
Cumarebo	0.7	0.8
Lagunillas Heavy	300.0	38.0
La Rosa Medium	230.0	24.0
Mara	220.0	18.0
Mototan #7	390.0	43.0
Taparito	450.0	40.0
Tia Juana Light	100.0	11.0
Tia Juana Medium	200.0	22.0
Tia Juana Heavy	300.0	25.0
Cachipo	14.0	3.3
Guanipa	110.0	27.0
Pedernales	230.0	87.0
Pilon	510.0	98.0
San Joaquin	0.6	0.2
Tigre	160.0	28.0
Tucupita	84.0	45.0

Baker, Earl W.: Vanadium and Nickel in Crude
Petroleum of South America and Middle East
Origin, Chem. and Eng. Data, 8, No 2, 306
(1964).

- (2) A large number of elements are found in the ash. In addition to the more common constituents listed in Table I, zinc, barium, strontium, tin, molybdenum, lead, copper, silver, uranium, and gold are found in trace amounts.
- (3) Vanadium and nickel are present in greater amounts than would be expected from consideration of the mineral environment of the crude⁽⁴¹⁾.

As mentioned previously, of the total ash-forming constituents in the crude when brought to the surface, some are considered to be associated with the origin of the oil. For example, some of the calcium was derived from animal bones, nickel compounds from seaweed, zinc from crustaceans, and vanadium from sea animals such as squirts and sea cucumbers⁽⁴¹⁾. The vanadium content of sea squirts may run as high as 0.65 per cent on a dry basis. A number of studies have shown that iron, nickel, and vanadium exist in crude oil as soluble, organometallic compounds, probably in a range of molecular weights.

The origin of vanadium in crude is of special interest because of problems introduced during combustion of the residual portion. Evidence derived from studies by Skinner⁽³⁸⁾ and others has demonstrated the presence of vanadium porphyrin in crude oil.

These nitrogen-containing vanadium complexes are soluble or dispersible in crude oil but are insoluble in water. They are stable to heat treatment in the presence of water at temperatures of 257 °F, but change their form or decompose at temperatures of about 340 °F. Although the porphyrin complexes are believed to exist in a range of molecular weights, the greater portion is of relatively high molecular weight and becomes concentrated in the residues of distillation. Data from absorption spectra⁽³⁸⁾ indicate that the structure of the complex is similar or perhaps identical to the vanadium complex of mesoporphyrin IX dimethyl ester. Figure 1 shows the structure of this complex.

The remainder of the ash-forming constituents in crude are inorganic in nature and insoluble in oil. A summary of the chemical forms of ash-forming elements believed to be present in crude is given in Table III⁽³⁾.

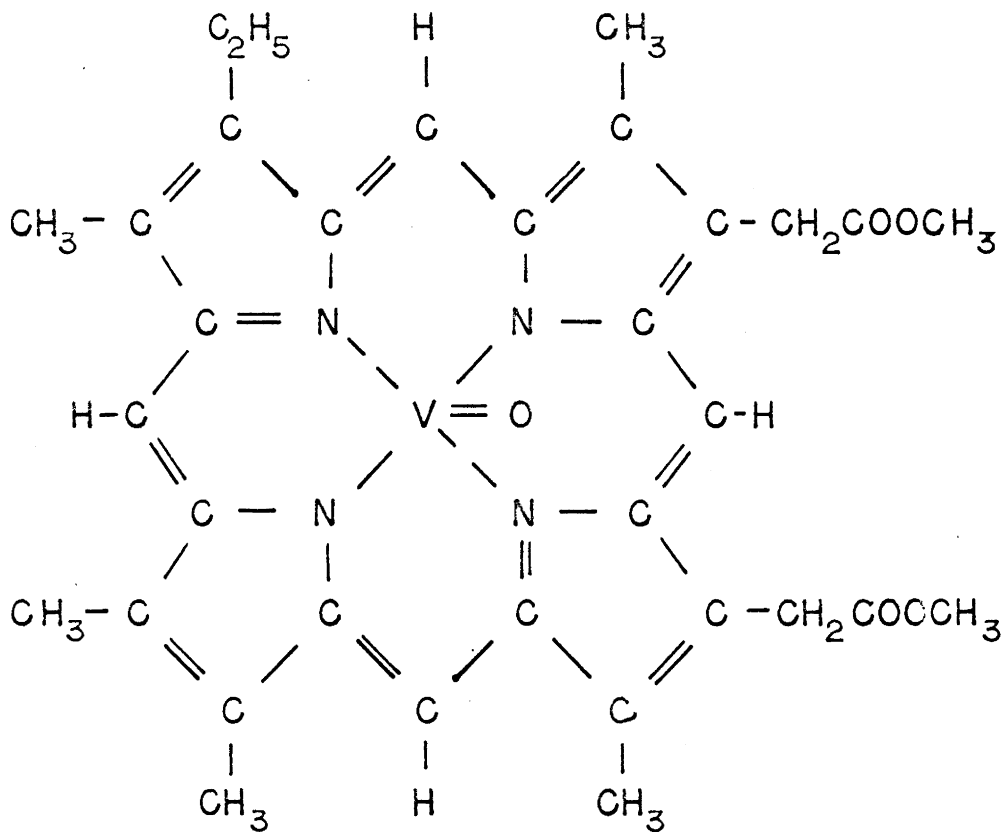


FIGURE I. PORPHYRIN MOLECULE

GRADY. H. R.: HOW VANADIUM CORROSION IS BEING COMBATED, OIL AND GAS J., 59, NO. 31, 173 (1961).

TABLE III

Principal Ash Forming Elements in Crude Oil

Element	Type	Solubility in Oil	Probable Chemical Form
Aluminum	Inorganic	Insoluble	Complex alumino-silicates
Calcium	Organic	Soluble	Unknown
	Inorganic	Insoluble	Calcium minerals and salts in suspension or dissolved in emulsified water
Iron	Organic	Soluble	Iron porphyrin complexes
	Inorganic	Insoluble	Iron oxides in suspension
Magnesium	Organic	Soluble	Unknown
	Inorganic	Insoluble	Magnesium salts in suspension or dissolved in emulsified water
Nickel	Organic	Soluble	Porphyrin complexes
Silicon	Inorganic	Insoluble	Complex silicates and sand in suspension
Sodium	Inorganic	Insoluble	Mostly sodium chloride in suspension or dissolved in emulsified water
Vanadium	Organic	Soluble	Porphyrin complexes
Zinc	Organic	Soluble	Unknown

Bowden, A. T., Draper, P., and Rowling, H.: The Problem of Fuel Oil Deposition in Open-Cycle Gas Turbines, Proc. Inst. Mech. Engr., 167, 296 (1953).

Removal of Ash Constituents. As problems involving corrosion and deposits developed in boiler and gas turbine units fired with residual oils, one of the first steps taken was to investigate possible ways to reduce the concentration of ash-forming constituents to a tolerable level, particularly with regard to reduction of vanadium and alkali metal compounds⁽²⁰⁾. However, because residual oils are by-products of a refining process designed primarily to produce the highest possible yields of gasoline and high-value distillates, their prices are in the range of competing low-cost fuels such as coal. Any additional processing costs to modify the properties of residual oil must be allocated either to increased prices for the residual oil or the high-value distillate fuels. Neither procedure can be economically justified. As long as all of the residual fuel can be disposed of somewhere on the market, further processing ordinarily cannot be justified.

A simple, low-cost treatment capable of removing a significant amount of undesirable ash constituents is difficult to find. Several attempts are discussed in following paragraphs.

Filtration. Suspended matter can be removed by filtration; however, oil soluble organometallic complexes containing vanadium are left in the crude⁽³⁷⁾.

Centrifuging. Processes involving centrifuging have been used with considerable success in preparing residual fuel for use in diesel engines, gas turbines, and marine plants^(5,11). Centrifuging alone will remove water from the fuel. If the water contains chlorides of sodium, magnesium, and calcium, these salts will be removed. If an emulsion is present, removal of water entails some loss of oil. When microcrystalline salts are present, a preliminary washing with water will provide removal, again with the formation of undesirable emulsions unless an effective emulsion-breaking compound is added to the fuel oil before washing. The oil soluble organometallic substances are not removed by centrifuging.

Treatment with Solvents. It is possible to separate most ash-forming constituents from fuel oil by treatment with selective solvents⁽³⁴⁾. The addition of certain solvents to residual oil precipitates the colloidal asphaltenes. Surface tension determines whether the asphaltenes are precipitated or brought into solution

in the solvent. Since the vanadium porphyrin complexes present in the oil are of relatively high molecular weight, it could be expected that they would be precipitated in substantial amounts with the asphaltenes.

Ion-Exchange. Interest has developed in recent years concerning the use of ion-exchange methods for demineralizing fuel oils, particularly for the removal of sodium and vanadium⁽¹⁸⁾. Wide ranges of experimental conditions were studied, but the attempts were unsuccessful.

Iodine Precipitation. A process for the removal of vanadium and nickel from crude oil by the addition of iodine has been developed⁽²⁰⁾. A precipitate is formed, which can be filtered. Apparently the iodine changes the oil-soluble vanadium complex into an insoluble one.

Additives for Preventing Corrosion. Since the slags do not accelerate corrosion until they are molten, many investigators^(2,10,16,22,33,40) have recommended the addition of oxides, carbonates, or sulfates of magnesium, calcium, aluminum, silicon, and tungsten to increase the melting point of the vanadium containing

slags. This technique does reduce corrosion; however, the increased ash builds up rapidly and limits boiler operating time between shutdowns for cleanup.

Ash Formation During Combustion. The combustion of a single atomized droplet of oil begins with the evaporation and ignition of the lighter hydrocarbons. This is followed by decomposition of the heavier hydrocarbons and, finally, the combustion of the residual carbon matrix. Because the temperatures reached during the decomposition stage are relatively high, a portion of the inorganic compounds which have high vapor pressures at these temperatures are vaporized. Sodium chloride, in particular, is vaporized in this manner. Its vapor pressure is about 10 millimeters of mercury at 1800 °F, while vanadium pentoxide is slightly less than 0.3 millimeter of mercury at the same temperature.

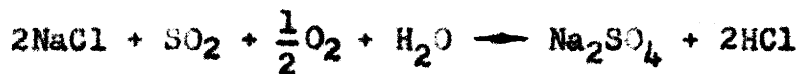
Most ash-forming compounds other than sodium chloride become concentrated in the carbon residue of the burning particle. During combustion, ash particles of the metallic oxides are formed. The organic vanadium complexes in the oil are decomposed, and the vanadium is oxidized first to the stable and

non-volatile forms vanadium trioxide and vanadium tetroxide, and finally to vanadium pentoxide. According to Sulzer and Bowen⁽³⁾, the vanadium pentoxide stage is formed only after the residual carbon particles have been completely consumed. The vanadium pentoxide is much less volatile than the sodium chloride, but its vapor pressure at high temperatures is sufficient that some is vaporized as free vanadium pentoxide. More of the vanadium pentoxide would be vaporized if it were present alone; however, with other metal ash constituents present such as iron, nickel, sodium, and calcium, various reactions take place with the vanadium oxides to form a series of vanadates. The vapor pressures of all of these compounds are lower than that of vanadium pentoxide.

The sulfur in oil is oxidized during the combustion process to sulfur dioxide and sulfur trioxide. Sulfur dioxide, then, is present in the gas stream at all times, usually in amounts more than sufficient to convert all of the metal oxides to sulfates and sulfites. However, not all metals form sulfates readily by reaction with sulfur dioxide, and the

sulfites and some sulfates are unstable at these temperatures. During the final combustion of the carbon in the original fuel droplet, high temperatures do not permit sulfate-forming reactions to occur.

In the following stage, however, during passage of the combustion gases from flame zone toward cooler sections (2550 to 1290 °F) of the boiler or turbine combustor, the conditions are suitable for reactions of small ash particles and vaporized ash constituents with sulfur dioxide and sulfur trioxide. Sodium chloride, for example, reacts with sulfur dioxide in the following manner:



The reaction is strongly exothermic. Sodium sulfate has a low vapor pressure and is carried with the gas in the form of fine particles.

Leaving the flame region, a large number of inorganic ash constituents consisting of oxides of vanadium, calcium, iron, nickel, magnesium, aluminum, and silicon, oxides of other elements in trace amounts, vaporized sodium chloride and vanadium pentoxide, sulfates such as sodium sulphate, some silicates, and

probably, some of the vanadates are entrained in the combustion gases. Some ash particles are melted and plastic, others are solid and refractory. The type and amount of each constituent will vary widely according to the source of the oil. A list of compounds prepared by Bowden, Draper, and Rowling⁽³⁾ which may be formed during combustion of heavy fuel is shown in Table IV.

Nature of Deposits from Heavy Fuels

Deposit problems in oil fuel systems result chiefly from the use of residual fuels made from Venezuelan and Middle East crudes. These crudes have relatively high sulfur and vanadium content, which is concentrated in the residual fuel by the refining process. During combustion, sulfur and vanadium oxides are formed, and in the presence of alkali and alkaline earth oxides and salts, the oxides are converted to sulfates, vanadates, and related compounds that appear as deposits in boilers and gas turbines.

Sulfate Deposits. Deposits in the high-temperature section of a boiler generally exhibit a transition in

TABLE IV

Possible Ash Constituents Formed During Combustion and
Their Melting Points

Compound	Melting Point °F
Al_2O_3	3720
$Al_2(SO_4)_3$	Decomposes at 1418 to Al_2O_3
CaO	4662
$CaSO_4$	2642
Fe_2O_3	2849
$Fe_2(SO_4)_3$	Decomposes at 896 to Fe_2O_3
MgO	4532
$MgSO_4$	Decomposes at 2055 to MgO
NiO	3794
$NiSO_4$	Decomposes at 1544 to NiO
SiO_2	3128
Na_2SO_4	1616
$NaHSO_4$	482 ^a
$Na_2S_2O_7$	752 ^b
V_2O_3	3578
V_2O_4	3578
V_2O_5	1247
ZnO	3270
$ZnSO_4$	Decomposes at 1364 to ZnO
$Na_2O \cdot V_2O_5$	1166
$2Na_2O \cdot V_2O_5$	1184
$3Na_2O \cdot V_2O_5$	1562
$2NiO \cdot V_2O_5$	1650
$3NiO \cdot V_2O_5$	1650
$Fe_2O_3 \cdot V_2O_5$	1580
$Fe_2O_3 \cdot 2V_2O_5$	1571
$Na_2O \cdot V_2O_4 \cdot 5V_2O_5$	1157
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$	995

^a Decomposes at about 480 °F to $Na_2S_2O_7 + H_2O$.

^b Decomposes at about 860 °F to $Na_2SO_4 + SO_3$.

Bowden, A. T., P. Draper, and H. Rowling: The Problem of Fuel Oil Deposition in Open-Cycle Gas Turbines, Proc. Inst. Mech. Engr., 167, 296 (1953).

properties and appearance from burner end to the rear of the furnace. Clarke⁽⁶⁾ and Collins^(7,8) both have found that the light colored granular deposits that occur at the burner end are high in both sodium and sulfate. They are hygroscopic to such an extent that free sulfuric acid has been observed by Slotter and Parr⁽³⁹⁾ during shutdown of marine boilers having this type of deposit. The sulfate deposits are soluble in water up to 90 per cent, and the resulting solution is extremely acid. There is a gradual transition in the composition of the deposits as the rear tubes are approached, with less sulfate and lower acidity.

An extreme case of sulfate separation was reported by McCoy⁽²⁵⁾ who found 13.2 per cent sodium oxide and 30.2 per cent sulphur trioxide in deposits from the radiant sections of a boiler, but none of either in the superheater deposits.

The rear tubes usually have layered deposits, with vanadium being concentrated in the inner layer and sodium sulfate predominating in the outer layer. The existence of sodium sulfate as such in the deposits has been verified by x-ray diffraction studies of the fireside deposits from some U. S. Navy

vessels⁽³²⁾. Minor amounts of the sulfates of other metals are undoubtedly also formed in the deposits; however, it is generally agreed that sodium sulfate is the chief agent in the fouling of oil fired boilers.

Table V shows data⁽⁶⁾ on the composition of a typical bi-layered deposit where vanadium is concentrated near the tube while sulfates predominate in the outer layer.

Vanadate Deposits. The relatively large amount of vanadium which occurs in many residual oils accounts for a large portion of the deposits in oil-fired systems. Vanadium was found by Clark⁽⁶⁾ in the compact, black, crystalline deposits on the high-temperature rear tubes of a marine boiler, in a form which he believed to be one of the lower oxides of vanadium. Whenever a two layer deposit occurs, the vanadium rich, black layer is found adjacent to the tube. In the form vanadium pentoxide, the vanadium has been reported in deposits on the final stage of a gas turbine, as shown by x-ray analysis⁽³⁰⁾; however, it is more common to find the vanadium in combination with sodium, as a vanadate. Sodium vanadyl vanadates ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 - 11\text{V}_2\text{O}_5$) have been

TABLE V

Composition of Bi-layered Deposit in
an Oil Fired Boiler

Deposit Component	Inner Layer	Outer Layer
	Concentration, Weight Per Cent	
Na ₂ SO ₄	23.99	46.78
NaHSO ₄	8.92	26.36
CaSO ₄	--	6.73
MgSO ₄	--	4.85
NiO	1.03	2.62
V ₂ O ₄	57.21	5.16
Fe ₂ O ₃	0.36	2.95
SiO ₂	0.55	1.41
H ₂ O	0.97	0.59
CaO	--	0.12
MgO	--	1.23
NiSO ₄	--	3.14

Clark, F. E.: Vanadium Ash Problems in Oil Fired Boilers, J. Amer. Soc. Naval Eng., 65, 259 (1953).

observed in deposits on marine boiler tubes and in high-temperature regions of gas turbines. The vanadate deposits are characterized by low water solubility as compared to the sulfate deposits, one analysis showing 10 per cent of a soluble portion to be vanadium pentoxide as compared to 72 per cent of the insoluble portion⁽³²⁾.

Selectivity in the deposition of vanadium compounds was noted also by Floyd and Probert⁽²³⁾, as a typical analysis of gas turbine deposit showed 33 per cent vanadium pentoxide on a stator blade as compared to 45.2 per cent on a rotor blade, from oil ash containing 62 per cent vanadium pentoxide. Table VI gives a complete description of vanadium deposits as observed by Pfenninger⁽³⁰⁾ on turbine stages.

In addition to the occurrence of vanadium-containing deposits in boilers and turbines they have been observed in other types of oil-burning units. Vanadium was found by Pemberton and Bell⁽²⁹⁾ in amounts up to 30 per cent vanadium pentoxide in almost all parts of Haifa refinery furnaces burning Middle East crudes. The formation of an iron vanadate

TABLE VI

Characteristics of the Deposits from Turbine Blades

Deposit	First Stage of Turbine	Second Stage of Turbine
Approximate working temperature of stage	1120 °F	790 °F
Appearance	Rusty red to brown powder	Bright yellow to bright brown powder
Sintering temperature	1170 °F	1180 °F
Melting temperature	1280 °F	1273 °F
X-ray result	α -phase ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$)	β -phase (V_2O_5)
<u>Analysis</u>	<u>Per Cent</u>	<u>Per Cent</u>
Water soluble fraction	6.7	14.9
SO ₂	5.2	5.1
Na ₂ O	1.4	1.2
CaO	1.9	Traces
MgO	1.0	0.0
V ₂ O ₅	60.0	80.0
Fe ₂ O ₃	10.0	3.6
NiO	8.1	2.7
Al ₂ O ₃	0.0	0.0
SiO ₂	1.0	0.4

Pfenninger, H.: Experience in Service with Gas Turbines Using Heavy Fuel Oil, Proc. 4th World Petroleum Congress, Section VI/D, p. 275 (1955).

($\text{FeO} \cdot \text{V}_2\text{O}_3$) was detected by Schab⁽³⁶⁾, through x-ray diffraction analysis of deposits resulting from test rig combustion experiments at 1600 °F, using a modified residual fuel. In some instances, the vanadium compounds formed in the deposit could not be identified by x-ray methods, because there are no known diffraction patterns (ASTM data) that correspond to those observed^(6,35).

Phase Diagrams for V-Alkali Metal Systems. As can be seen from Figures 2 and 3 the addition of alkali metal oxides to vanadium pentoxide, particularly at a concentration of approximately 35 to 40 mol per cent alkali metal oxide, forms an eutectic with significantly lower melting point than the pure vanadium pentoxide. Most efforts to reduce corrosion have been directed at altering the system to raise the melting point of the slag⁽²¹⁾.

Work by Foster and associates⁽¹⁴⁾ with the system sodium sulphate-vanadium pentoxide, Figure 4, shows that heat-treated mixtures of these compounds cannot be regarded as simple mechanical mixtures. It was found that:

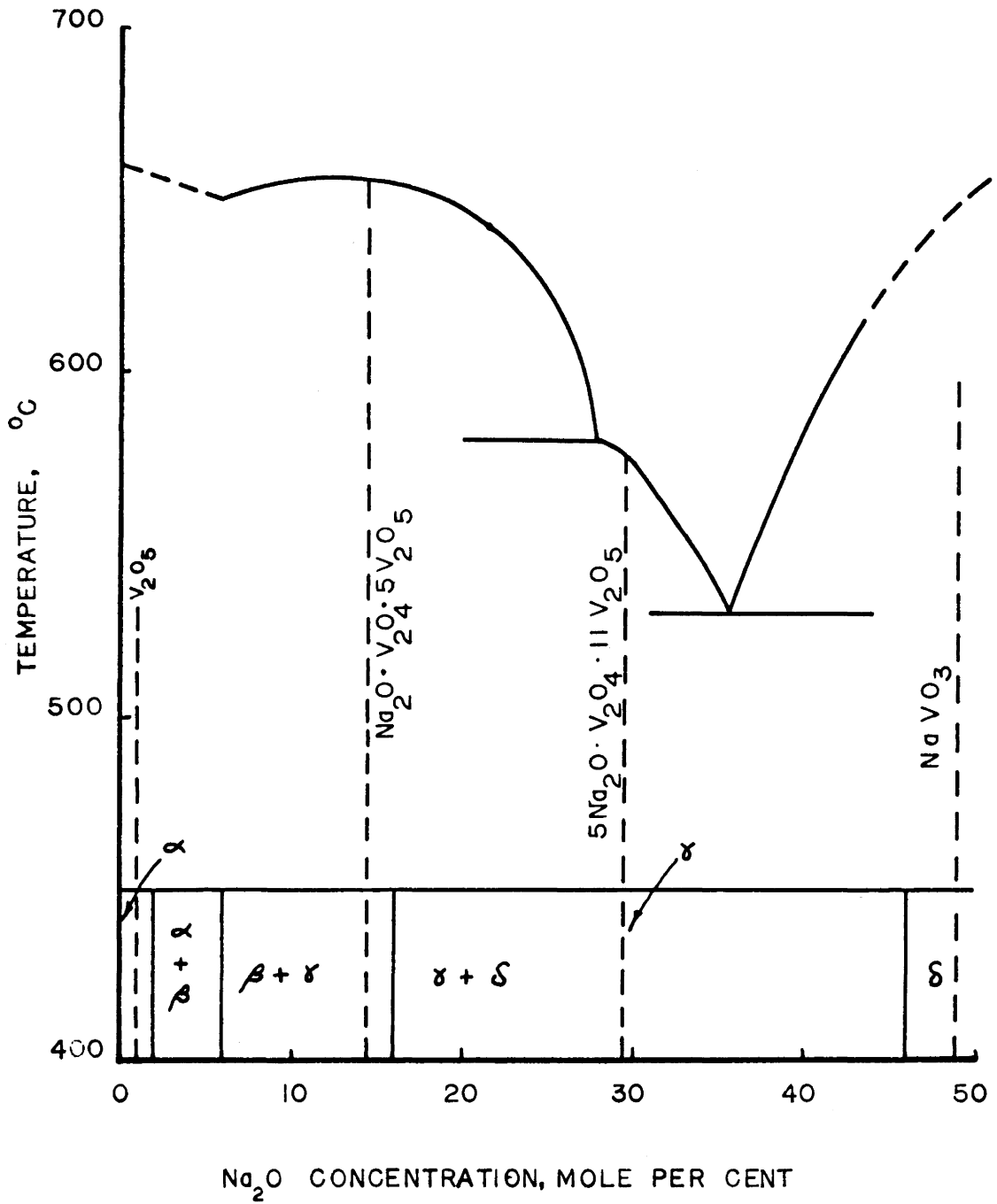


FIGURE 2. SODIUM OXIDE-VANADIUM PENTOXIDE PHASE DIAGRAM

LEVIN, E. M. AND H. F. MCMURDIE: "PHASE DIAGRAMS FOR CERAMISTS-PART II," P. 7, AMERICAN CERAMIC SOCIETY, COLUMBUS, OHIO, 1959.

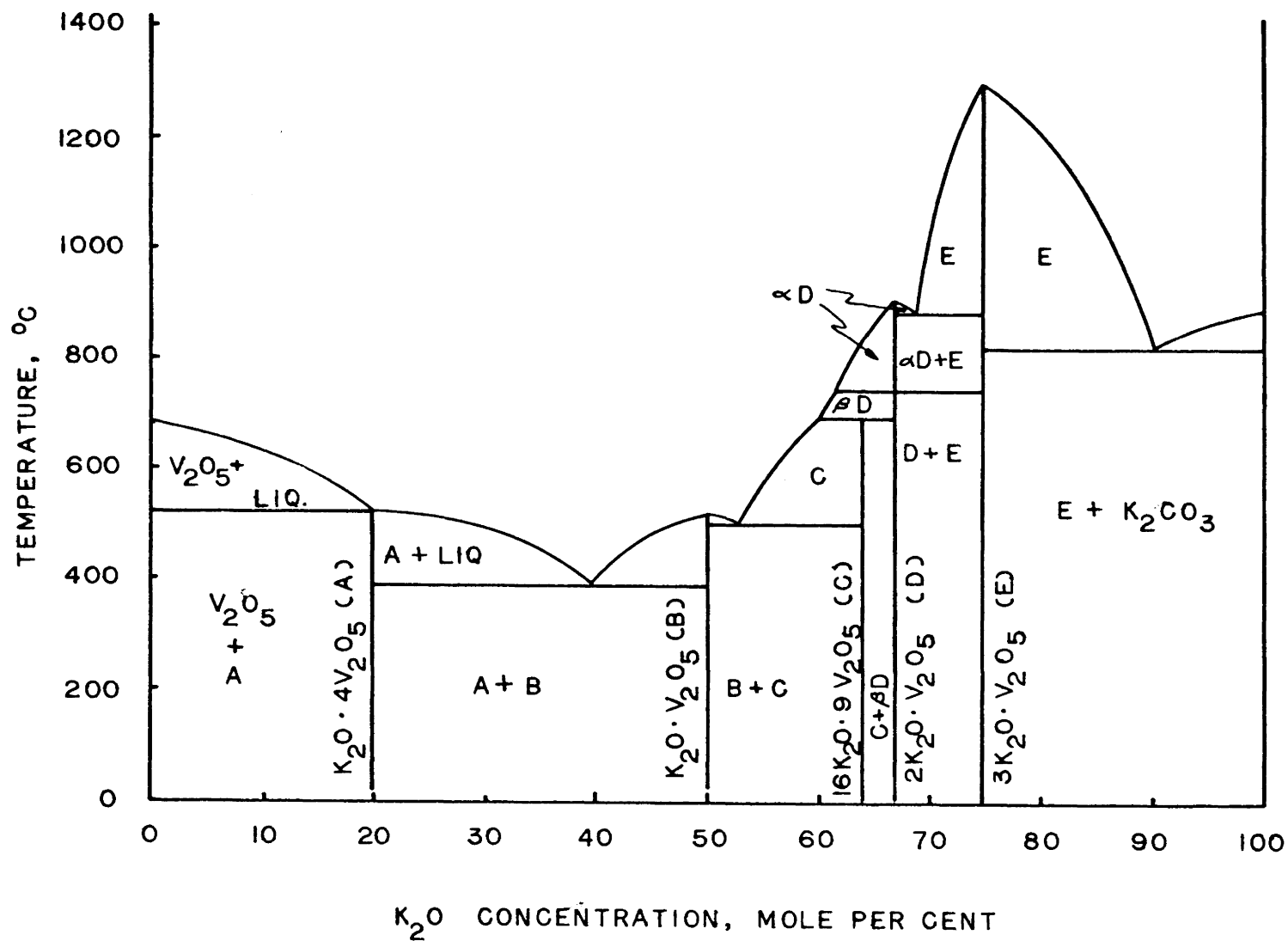


FIGURE 3. POTASSIUM CARBONATE-VANADIUM PENTOXIDE PHASE DIAGRAM

LEVIN, E. M. AND H. F. MCMURDIE: "PHASE DIAGRAMS FOR CERAMISTS-PART II," P. 9, AMERICAN CERAMIC SOCIETY, COLUMBUS, OHIO, 1959.

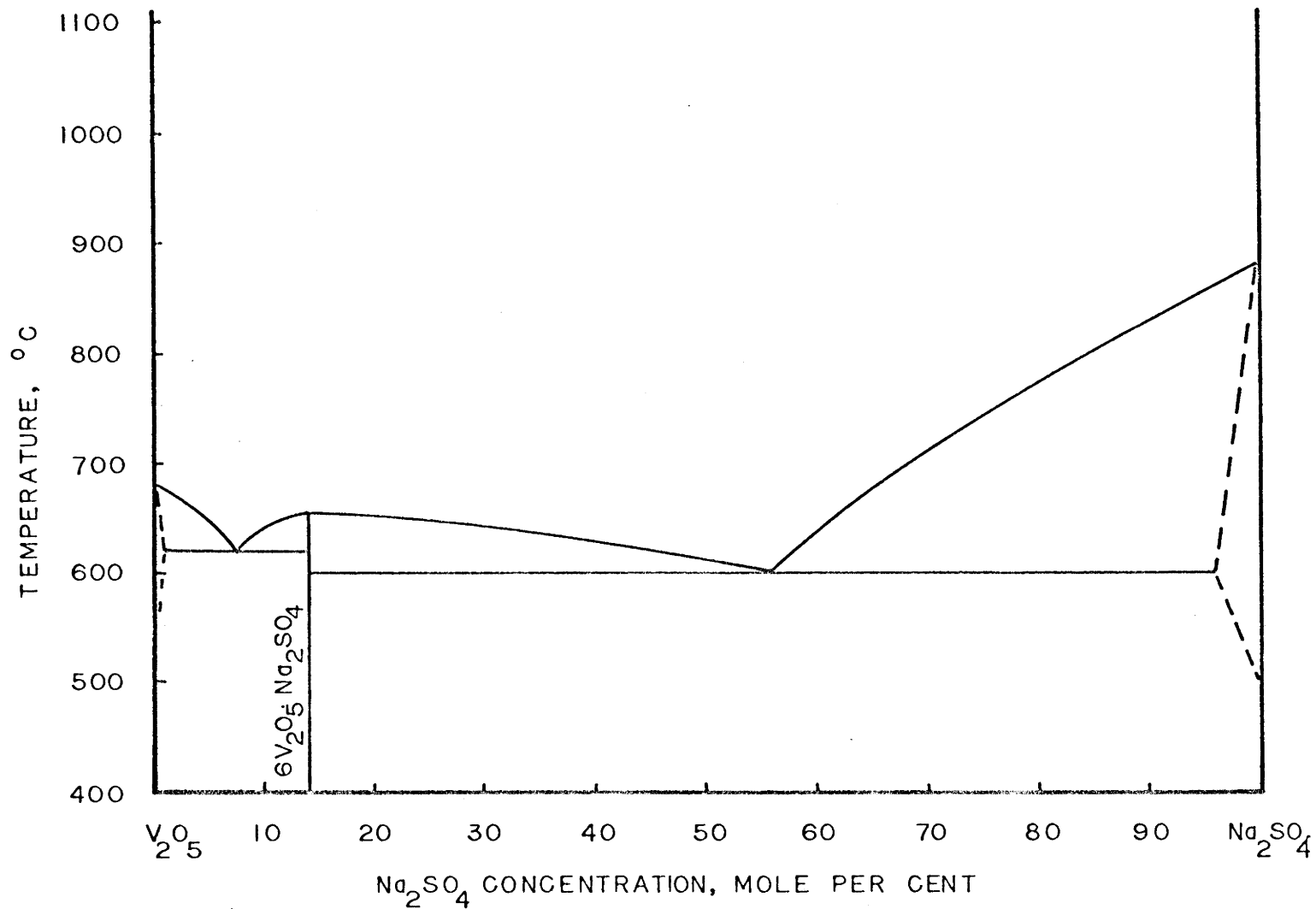


FIGURE 4. SODIUM SULPHATE-VANADIUM PENTOXIDE PHASE DIAGRAM

CUNNINGHAM, G. W. AND A. DES. BRASUNAS: THE EFFECTS OF CONTAMINATION BY VANADIUM AND SODIUM COMPOUNDS ON THE AIR-CORROSION OF STAINLESS STEEL, CORROSION, 12, 389T, (1956).

- (1) Sodium sulphate exists only in mixtures containing less than 56 per cent vanadium pentoxide.
- (2) Sulfur trioxide is liberated from all mixtures, partially up to 56 per cent vanadium pentoxide (at which the weight loss reaches a maximum of 24.5 per cent), and completely beyond 56 per cent vanadium pentoxide.
- (3) The 56 per cent vanadium pentoxide mixture consists entirely of sodium vanadate.
- (4) The 80 per cent vanadium pentoxide mixture consists entirely of the complex having a sodium to vanadium ratio of 1/3.
- (5) The 88.8 per cent vanadium pentoxide mixture consists entirely of the complex sodium vanadyl vanadate ($\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$).
- (6) Free vanadium pentoxide exists only in mixtures containing in excess of 88.8 per cent vanadium pentoxide.

Corrosion by Vanadium Containing Deposits

In a number of recent investigations of oil-ash corrosion of metals, a simplification of the analysis of the problem has been sought through a study of the effects of a series of mixtures of sodium sulfate and vanadium pentoxide^(4,9,13,28). In view of the predominance of sodium, sulfur, and vanadium in typical ashes such simplification would appear to be justified; however, even the numerous studies of these simplified ashes have not resulted in a consistency of view as to the specific agents of corrosion. In some instances corrosion has been attributed to either or both of the end members (sodium sulphate and vanadium pentoxide). In others, corrosion has been blamed on certain complex sodium vanadates.

Slag Composition. Most recent investigations^(1,14,17,25,28) have found the low-melting sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, to be the most corrosive slag substance. This compound may be formed in the slag even when the sodium to vanadium ratio is 1:1. Not only is the compound corrosive, it is an excellent flux.

These complexes evolve oxygen upon being cooled from the liquid to the solid state due to the reversible change of the acid vanadate to the vanadyl vanadate.

The corrosion of Alloy JA-5, a stainless steel containing: 0.056 per cent carbon, 18.15 per cent chromium, 9.18 per cent nickel, 0.40 per cent silicon, and 1.13 per cent manganese, by various mixtures of sodium sulphate and vanadium pentoxide at 1650 °F in air was determined by Cunningham and Beasunas⁽¹⁰⁾. The results of this work are shown in Figure 5.

Atmosphere Composition. Most studies to date have been conducted in air or oxygen. Several investigators^(17,19) have stated that oxygen in the surrounding atmosphere was necessary for corrosion to take place and some have used oxygen consumption as a measure of corrosion rate. Logan⁽²⁵⁾ states that catastrophic corrosion takes place in the presence of moist air but not in the presence of dry air or moist helium. Greenert⁽¹⁷⁾ found no corrosion at temperatures up to 1700 °F in a nitrogen atmosphere.

Composition of Corrosion Products. Investigators^(1,17) have identified complex nickel vanadates ($NiO \cdot V_2O_5$ and $2NiO \cdot V_2O_5$), chromium vanadate, complex

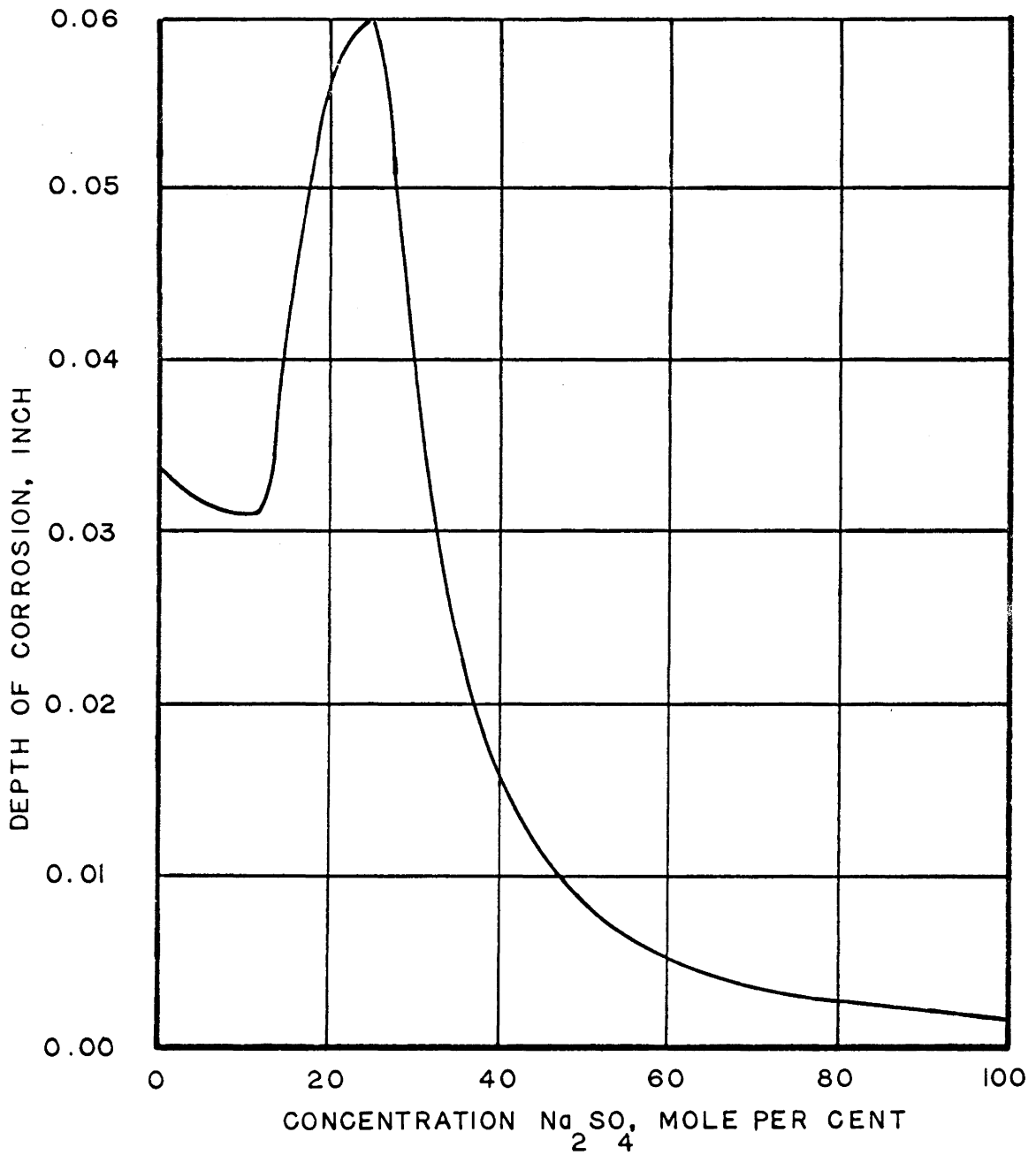


FIGURE 5. EFFECT OF COMPOSITION OF VANADIUM PENTOXIDE-SODIUM SULPHATE MIXTURE ON THE AIR-CORROSION OF ALLOY JA-5 AT 1650 °F

CUNNINGHAM, G.W. AND A. DES. BRASUNAS: THE EFFECT OF CONTAMINATION BY VANADIUM AND SODIUM COMPOUNDS ON THE AIR-CORROSION OF STAINLESS STEEL, CORROSION, 12, 395T (1956).

ferric vanadate ($\text{Fe}_2\text{O}_3 \cdot 2\text{V}_2\text{O}_5$) and possibly the iron vanadate (FeVO_4) in the products of corrosion of chrome-nickel steels by mixtures of sodium sulphate and vanadium pentoxide. X-ray diffraction data indicate that many unidentifiable compounds are also present.

Suggested Corrosion Mechanisms. The following mechanisms have been suggested for the accelerated oxidative effect of vanadates ⁽¹⁾:

- (1) Vanadates act as oxygen carriers.
- (2) Molten vanadates dissolve or destroy the normally protective oxide layer.
- (3) The vanadate distorts the normally stable lattice structure of the metal oxide allowing relatively easy transport of metal ions or oxygen to or from the oxide deposit interface.

Results of electron probe microanalysis have shown that vanadium, although present in the deposit layer, was not found in the oxide adjacent to the metal. Thus, there is doubt about the possibility of mechanism 3.

III. EXPERIMENTAL

The following section contains the purpose of this investigation, the plan of experimentation, the materials and apparatus used, the method of procedure, the data and results, and the sample calculations.

Purpose of Investigation

The purpose of this investigation was to study the corrosion of 1020 carbon steel, stainless steel 347, Hastelloy X, and Hastelloy B at temperatures between 650 °C and 980 °C in the presence of a mixture of sodium carbonate and vanadium pentoxide, and to attempt to establish the corrosion reactions which take place at these conditions.

Plan of Experimentation

The experimental plan which was followed in this investigation consisted of a review of the literature, assembly of equipment, experimental work, and analysis of results.

Literature Review. A review of the literature was made to familiarize the author with the principles of corrosion and the state of the art as applied to high temperature corrosion in the presence of metal salts. The primary sources of information for this literature search were the "Chemical Abstracts" and "Industrial Arts Index." The bibliographies of the articles located through these publications were used to increase the scope of the review.

Assembly of Equipment. The equipment for this investigation consists of a tube furnace capable of heating the corrosion specimens to 927 °C for sustained periods of time, plus such additional equipment as required to control the atmosphere around the specimens and to control and measure the temperature of the specimens.

Experimental Work. Before investigating the nature of the corrosive attack on alloys by sodium carbonate and vanadium pentoxide at high temperatures, preliminary tests were made to establish experimental techniques and obtain necessary background information. Tests were made to develop procedures for cleaning the specimens, for preparing the salt, for coating the

specimens with the salt, and for removing and analyzing the corrosion products from the specimens.

After completion of the work required to establish procedures, corrosion tests were made on four alloys: 1020 carbon steel, stainless steel 347, Hastelloy X, and Hastelloy B. These alloys were chosen because they contain varying amounts of the high temperature alloying agents--chromium and nickel. Specimens of each alloy were (1) coated with various mixtures of sodium carbonate and vanadium pentoxide, (2) placed in an atmosphere of either carbon dioxide or helium, and (3) maintained at a constant temperature in the range of 593 °C to 927 °C for periods of time ranging from 6 to 36 hours.

The corroded specimens were cleaned and weighed to determine loss in weight, and the material removed from the specimens was analyzed to determine the composition of the products of corrosion. X-ray techniques were used to analyze the corrosion products.

Analysis of Results. The data obtained from this investigation were analyzed in an effort to (1) postulate a reaction for the corrosive attack of molten mixtures of sodium carbonate and vanadium pentoxide

on the various alloys tested, (2) determine the effect of an oxidizing atmosphere, carbon dioxide, on the rate of corrosion, and (3) determine the effect of nickel and chromium on the rate and type of corrosion.

The study provided data on weight loss versus time for the steels investigated at various temperatures, in both oxidizing and reducing atmospheres, for various slag compositions. Data on composition of corrosion product was also obtained. These data were analyzed in an effort to determine kinetic parameters of the reactions which will be helpful in postulating reaction mechanisms and determining whether different mechanisms occur at the different test conditions.

The data and results from this investigation will also provide information on the relative resistance of the alloys tested to the corrosive attack of a mixture of sodium carbonate and vanadium pentoxide at the conditions of the tests and possibly lead to a method for eliminating or reducing this corrosion problem.

Materials and Apparatus

The metal specimens used in this investigation were cut from commercial grade, 0.05 inch thick 1020 carbon steel, Hastelloy B, Hastelloy X, and 347 stainless steel. The ladle analysis for the 1020 carbon steel is shown in Table VII. The chemicals used to prepare the slags were Baker "Analysed" and Fisher "Certified" reagents.

Detailed descriptions of all materials and apparatus are given in Appendix I.

Methods of Procedure

The procedures used in this investigation are presented in this section under the headings

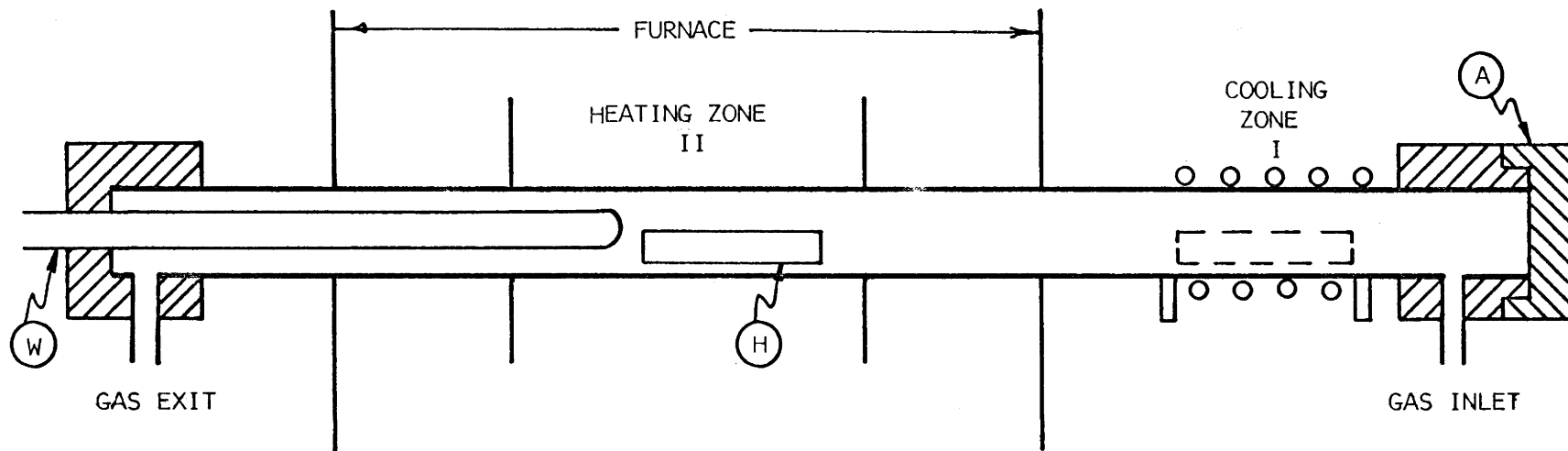
- (1) calibration for specimen temperature and
- (2) corrosion test procedure.

Calibration for Specimen Temperature. For the arrangement shown in Figure 6, it is obvious that the temperature measured by the thermocouple in thermowell W was not the same as the specimen temperature. Since the thermocouple in thermowell W was used to control the furnace temperature, a correlation between it and

TABLE VII

Ladle Analysis of 1020 Carbon Steel Heat G-3152

Element	Concentration Weight Per Cent
Carbon	0.190
Manganese	0.410
Phosphorus	0.008
Sulphur	0.029



-40-

LEGEND

- A - CAP
- H - SAMPLE HOLDER
- W - THERMOCOUPLE WELL

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SCHMATIC OF THE
 COMBUSTION TUBE

SCALE: NONE FIGURE: 6
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the specimen was required. To obtain this correlation, an iron-constantan thermocouple was attached to the surface of two specimens, the specimens were placed in a nickel combustion boat as they would be in a standard test and placed in the furnace; one sample in each tube. The thermocouple leads were insulated with ceramic insulators and brought out through the tube entrance. The furnace was controlled at various temperatures and the electromotive forces generated by the thermocouples attached to the surface of the specimens were measured with a potentiometer. An ice bath was used as the reference junction. The temperature measured by the thermocouple in thermowell W was controlled and recorded by the recorder-controller.

Corrosion Test Procedure. The corrosion test procedure consisted of sample preparation, slag preparation, coating samples with slag, heating, cleaning, and weighing. Each of these topics is discussed in detail in the following sections.

Sample Preparation. Metal specimens approximately 0.5 x 0.75 inch were cut from 0.05 inch thick stock with a water cooled cut-off saw. The cuts were made

slowly and large quantities of cooling water were used to prevent excessive heating of the edges of the specimen. The edges of the specimens were rough polished with fine emery cloth and finished polished with 400A polishing paper.

The polished specimens were scrubbed with soap and water, washed with acetone, and cleaned according to type metal in the following acid baths⁽⁴³⁾: for 1020 carbon steel, 49.0 per cent concentrated hydrochloric acid, 49.0 per cent water, and 2.0 per cent Rodine 120; for Hastelloy X, 31.0 per cent concentrated nitric acid, 6.5 per cent concentrated hydrofluoric acid, and 62.5 per cent water; and for Hastelloy B and 347 stainless steel, 27.5 per cent hydrochloric acid, 6.4 per cent nitric acid, 64.0 per cent water, and 2.1 per cent sodium bichromate. The Hastelloy X samples were left in the acid bath for a minimum of 30 minutes. All other metals were pickled for a minimum of four hours. After pickling, the specimens were again scrubbed with soap and water, washed with acetone, and dried.

The length and width of each specimen were measured with a caliper and the sample was weighed on an analytical balance. The specimens thus prepared

were immediately coated with slag and placed in the oven for a corrosion test. Coated samples not placed immediately in the oven were stored in a desiccator.

Slag Preparation. The slags used in these tests were composed of sodium carbonate and vanadium pentoxide. The dry ingredients were weighed into a 50 milliliter nickel crucible on an analytical balance, mixed, and melted in a Hoskins furnace. The nickel crucible was placed in a ceramic crucible to protect the furnace from splashes and spills. All samples were held at 982 °C for one hour, and then cooled to room temperature. The slag was then remelted in the Hoskins furnace for application to the metal specimens.

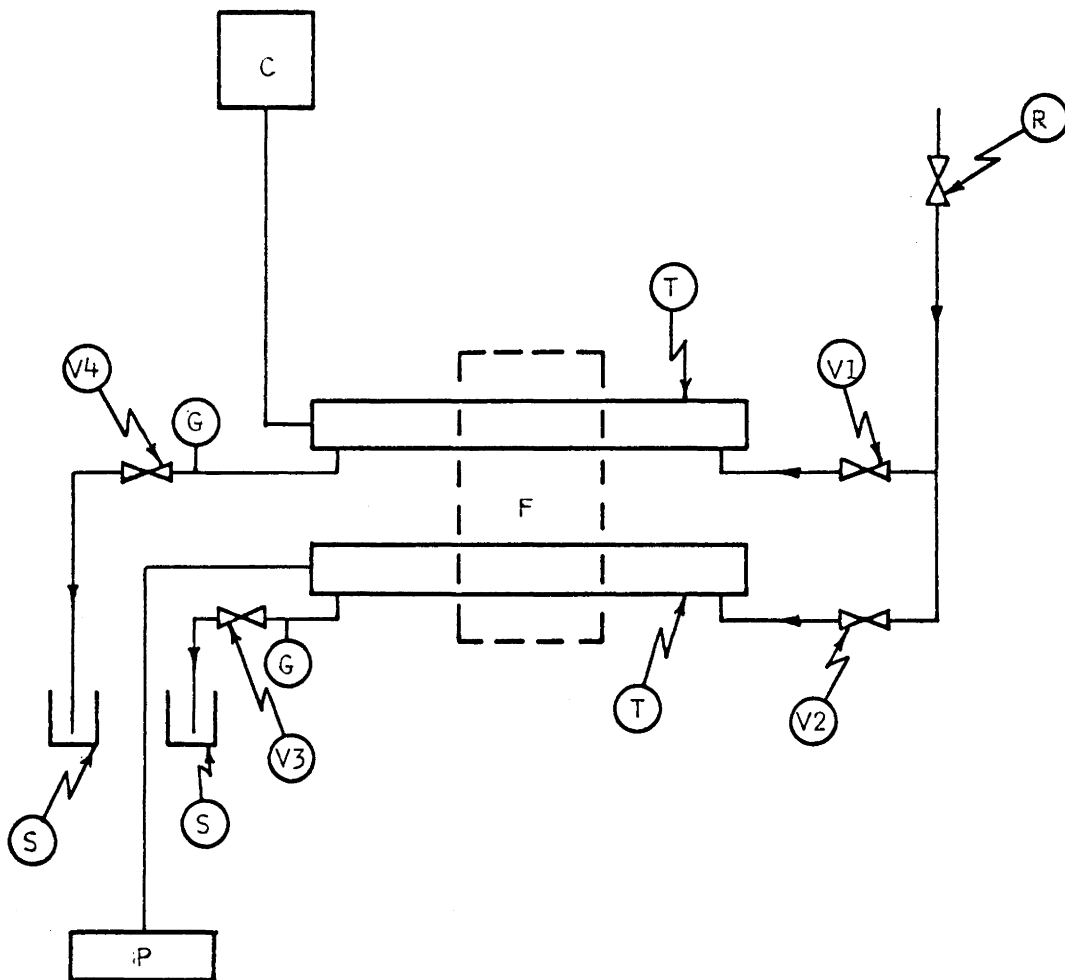
Coating Specimen with Slag. To coat the metal specimens, they were held by one end with tongs and dipped into the molten slag such that at least two-thirds of the specimen was coated. The partially coated sample was allowed to cool until the slag deposit hardened. The sample was picked up by the coated end and the remainder of the sample coated. The slag applications were overlapped to insure complete coverage of the specimen. In selected cases

the coated sample was weighed to determine the amount of slag applied.

Heating the Specimen. To allow the slag and the metal specimen to react at a controlled temperature in a known atmosphere, the slag coated specimens were placed in a nickel combustion barge in a combustion furnace. Either helium or carbon dioxide flowed through the combustion tubes while the tests were in progress. The procedure followed is outlined below. All references are to Figure 7 or Figure 6, page 40.

To prepare the furnace, the desired temperature was set on the recorder controller C, and sufficient time was allowed for the temperature to level out. Simultaneously, the desired gas, either carbon dioxide or helium, was connected at point R and by opening valves V-1 and V-2 allowed to flow through the system, purging the lines and furnace tubes.

A standard test series consisted of eight specimens, four in each of two combustion barges, one barge in each furnace tube. When the furnace temperature became constant and the system was purged with the desired gas, the barges were placed in the furnace. To reduce the amount of air carried into the furnace with the



LEGEND

- C - RECORDER-CONTROLLER
- F - FURNACE
- G - PRESSURE GAGE
- P - POTENTIOMETER
- R - REDUCING VALVE
- S - WATER SEAL
- T - COMBUSTION TUBE
- V - VALVE

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SCHEMATIC OF THE
CORROSION APPARATUS

SCALE: NONE FIGURE NO: 7

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specimens, the gas flow to the tube was increased before the end cap A was removed. The increased gas flow and the water seal S at the exit end of the tube caused gas to flow out of the tube entrance thus preventing air flow into the tube. The combustion barge was placed in zone I in the tube, the end cap A was replaced, and the tube was purged for 30 seconds. The end cap was removed again and the barge was moved to zone II, the heating zone of the furnace. After replacing the end cap, the tube was purged for an additional 30 seconds. The gas flow was then adjusted by valves V-1 and V-2 to give approximately 20 bubbles per minute from the exit water seal S.

To remove a specimen from the furnace, the gas flow was increased by opening valves V-1 and V-2, the end cap A was removed, and the combustion barge was moved to zone I, the water cooled section of the tube. The end cap A was replaced and the barge and samples were cooled for one minute. The end cap was removed again, the barge was slipped out of the tube, and the desired sample(s) were removed. The barge and remaining samples were then replaced in the furnace using the procedure followed at the start of the test.

During the test the furnace temperature as measured by the thermocouple in the thermowell W was recorded continuously by the recorder controller C. As an additional check the thermocouple in the second tube was connected to a potentiometer P and the temperature was measured periodically.

An attempt was made to eliminate the effect of tube to tube variation and position within a tube by varying the sample plan from test to test. Duplicate samples were taken such that: (1) both were in the same tube, (2) each in different tubes, (3) both corroded during same time period, and (4) each corroded during different time periods.

Cleaning and Weighing. After being corroded by the molten slag it was necessary to clean the corrosion products from the metal specimen. In the case of the 1020 carbon steel samples this was accomplished by cleaning with the same acid mixture used for initial cleaning and described in the section on Sample Preparation. Although this acid mixture attacks 1020 carbon steel only slightly, it was believed this attack should be taken into consideration; therefore,

a correction was determined for each test specimen.

Two techniques were employed.

The first technique consisted of placing a corroded sample in a beaker containing the acid solution. The corroded sample was removed periodically and examined. If it appeared clean it was scrubbed with soap and water, dried with acetone, weighed on an analytical balance, and returned to the acid solution. After a minimum of two hours, the sample was again removed and weighed. This process was repeated until the rate of weight loss per unit area of sample was constant.

The average rate of corrosion of a clean specimen of 1020 carbon steel in the acid mixture was determined. This rate multiplied by the length of time required to clean the specimen was subtracted from the uncorrected weight loss to obtain the actual weight loss by slag corrosion.

It was found that cleaned specimens, after being corroded, lost weight at a lower rate in the cleaning bath than blank specimens which had not been heated. To eliminate this source of error, a second technique was developed, in which the cleaned specimen was used as its own blank. The corroded specimen was placed in

the acid cleaning bath. The specimen was removed periodically and examined. If it appeared clean, the time was recorded; the sample was scrubbed with soap and water, dried with acetone, weighed on an analytical balance, and returned to the acid bath. This process was repeated until the weight loss per hour became constant. Knowing the total time in the cleaning bath and the corrosion rate of the cleaned specimen, a correction weight loss was calculated. The correction weight was subtracted from the total weight loss of the specimen to give the actual weight loss by slag corrosion. The second technique is considered the most accurate.

To remove the products of corrosion from the Hastelloy X, Hastelloy B, and 347 stainless steel specimens, a corroded specimen was dipped in molten sodium carbonate. The bulk of the sodium carbonate was then broken from the specimen and the residue was removed with the same acid bath used to clean the 1020 carbon steel specimens. The specimen was then scrubbed with soap and water, dried with acetone, and weighed with an analytical balance. This process was repeated to assure that the specimen was thoroughly cleaned.

Since neither the molten sodium carbonate nor the hydrochloric acid pickling solution significantly attacked any of these steels, no blank was used.

Corrosion During Preparation and Cleaning. To determine if the metal specimens were corroded during slag coating operations and to determine the validity of the cleaning correction techniques, samples were prepared, coated with slag, and cleaned. The corrected weight loss for these specimens should be approximately zero if the techniques employed are correct.

Corrosion in the Absence of Slag. To determine the effect of helium and carbon dioxide on the bare metal surfaces in the absence of slag, samples of 1020 carbon steel, Hastelloy X, Hastelloy B, and 347 stainless steel were processed as described previously with the exception that the specimen was not dipped into the slag. Tests were conducted at temperatures from 593 °C to 927 °C.

Effect of Temperature. To determine the effect of temperature on the corrosion rate, samples of 1020 carbon steel, Hastelloy B, Hastelloy X, and 347 stainless steel were coated with a 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag, and

processed as described previously at temperatures of 593 °C, 677 °C, 760 °C, 843 °C, and 927 °C in both helium and carbon dioxide atmospheres.

Effect of Slag Composition. To determine the effect of slag composition on the corrosion of 1020 carbon steel, samples were coated with vanadium pentoxide-sodium carbonate slags containing 16, 36, 50, 90, and 100 mole per cent sodium carbonate and processed as described previously in both carbon dioxide and helium atmospheres at a temperature of 927 °C.

Effect of the Addition of Fresh Slag. To obtain additional proof that a component of the slag was reacting with the metal and to prove that continuous addition of slag would result in the corrosion of the metal specimen at a high rate, samples of 1020 carbon steel were coated with an 84 mole per cent vanadium pentoxide slag and placed in a carbon dioxide atmosphere at 927 °C. At five hour intervals samples were removed and redipped in the slag. The specimens were not cleaned prior to redipping. Each time the specimens were removed from the furnace, one sample was cleaned to determine weight loss to that point.

Effect of Gas Pressure. To determine the effect of increased carbon dioxide concentration on the corrosion of the slag coated specimens, samples were corroded while maintaining pressures of 15 and 28 pounds per square inch, gage, in the combustion tubes.

Analysis of Corrosion Products. Since it is difficult to remove a sample of the slag from the specimens without damaging the specimen, certain selected samples were re-run for the specific purpose of removing the products of corrosion for analysis. X-ray diffraction patterns for the products of corrosion obtained in this manner were made.

Data and Results

This section of the report presents the data and results obtained during the course of this investigation.

Data for Relating Control Temperature to Actual Specimen Temperature in the Veritemp Combustion Furnace.

Since the temperature of the specimen and the temperature measured by the thermocouple used to control the furnace temperature were not the same, it was necessary to determine the relationship between these two temperatures. The data showing this relationship are presented in Table VIII, and are shown graphically in Figure 8. The actual specimen temperature was always higher than the controlled temperature by from 110 °C to 140 °C. The temperature in the left combustion tube was always higher than the temperature in the right combustion tube by an average of approximately 12 °C.

Corrosion During Preparation and Cleaning. Tests were made to determine if the samples were corroded during preparation, particularly during the slag coating operation, and to determine the accuracy of the cleaning correction procedure. The data from these tests are given in Table IX. In no case was the cleaned corrected weight significantly different from the initial

TABLE VIII

DATA FOR RELATING CONTROLLED TEMPERATURE TO ACTUAL
SPECIMEN TEMPERATURE IN THE VARITEMP
COMBUSTION FURNACE

CONTROLLED TEMPERATURE ^a °F	ACTUAL TEMPERATURE OF SPECIMEN ^b , °F	
	LEFT TUBE	RIGHT TUBE
800	983	1014
1000	1202	1228
1200	1415	1472
1400	1645	1657

^a TEMPERATURE AS RECORDED BY RECORDER-CONTROLLER WITH AUTOMATIC COLD END COMPENSATION.

^b TEMPERATURE MEASURED BY THERMOCOUPLE PEENED TO THE SPECIMEN SURFACE USING A POTENTIOMETER WITH ICE BATH COLD JUNCTION.

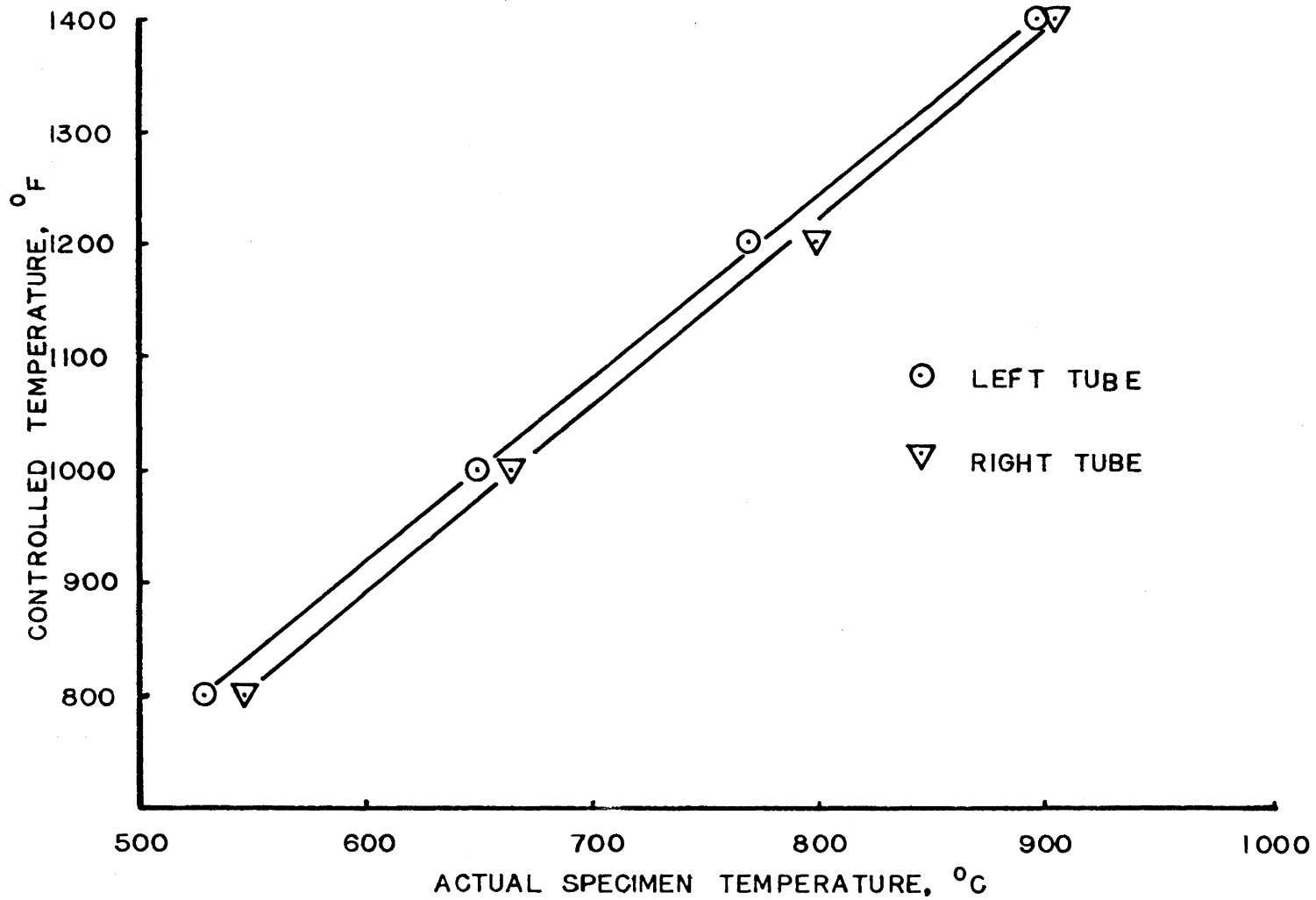


FIGURE 8. RELATIONSHIP BETWEEN THE TEMPERATURE OF THE METAL SPECIMEN AND THE CONTROLLED TEMPERATURE OF THE FURNACE

TABLE IX

CORROSION DURING PREPARATION AND CLEANING

SAMPLE DESCRIPTION	SAMPLE AREA	INITIAL WEIGHT	CORRECTED WEIGHT
	SQ IN	GM	GM
1020 CARBON STEEL 100 MOLE PER CENT Na_2CO_3 SLAG	0.868	2.3217	2.3214
1020 CARBON STEEL 90 MOLE PER CENT Na_2CO_3 SLAG	0.751	2.0059	2.0062
1020 CARBON STEEL 50 MOLE PER CENT Na_2CO_3 SLAG	0.882	2.3599	2.3598
1020 CARBON STEEL 36 MOLE PER CENT Na_2CO_3 SLAG	0.926	2.5205	2.5202
1020 CARBON STEEL 16 MOLE PER CENT Na_2CO_3 SLAG	0.853	2.2450	2.2448
HASTELLOY X 36 MOLE PER CENT Na_2CO_3 SLAG	0.935	2.4254	2.4256
HASTELLOY B 36 MOLE PER CENT Na_2CO_3 SLAG	0.998	2.8547	2.8544
347 STAINLESS STEEL 36 MOLE PER CENT Na_2CO_3 SLAG	0.974	2.1609	2.1611

specimen weight; therefore, corrosion during slag application is negligible and the cleaning correction technique employed is valid.

Weight of Slag Deposited on Specimen. The average weight of vanadium pentoxide-sodium carbonate slag adhering to 25 different steel specimens, determined by weighing the specimens before and after slag application, was found to be 1.35 grams per square inch of metal surface.

Corrosion of Apparatus by Slag. As evidenced by pitting of the nickel combustion boats and crucibles, the 304 stainless steel combustion tubes, and the 316 stainless steel thermocouple wells, the slag attacked all metal parts of the apparatus present in the heated zone.

As was the case with the metal specimens tested, the severity of the attack on the nickel crucibles increased as the vanadium pentoxide content of the slag increased. A nickel crucible containing pure molten vanadium pentoxide was completely destroyed in 30 hours.

This result indicates that materials more resistant to the slags tested are needed for the construction of the test apparatus.

Corrosion of 1020 Carbon Steel by a Forty-Nine Weight Per Cent Hydrochloric Acid Solution Inhibited with Two Weight Per Cent Iodine 120. Initially, an average cleaning correction factor of 0.39 milligram per square inch, hour, was used for all 1020 carbon steel samples. The data used to determine this correction factor are shown in Table X.

Corrosion in the Absence of Slag. To determine the relative effect of carbon dioxide and helium on the bare metal specimens, samples of 1020 carbon steel, Hastelloy B, Hastelloy X, and 347 stainless steel were exposed to each gas at temperatures from 593 °C to 927 °C. The results of these tests are shown in Table XI, and are expressed graphically in Figure 9 and Figure 10. The corrosion of 1020 carbon steel by carbon dioxide increases rapidly with temperature. Corrosion in the helium atmosphere is significantly lower than in the carbon dioxide atmosphere and the data are quite erratic. An Arrhenius plot for the corrosion of 1020 carbon steel by carbon dioxide is shown in Figure 11.

The corrosion of Hastelloy B, Hastelloy X, and 347 stainless steel by carbon dioxide at 927 °C was negligible.

TABLE X

CORROSION OF 1020 CARBON STEEL BY A 49 PER CENT HYDROCHLORIC
ACID SOLUTION INHIBITED WITH TWO PER CENT RODINE 120

TIME IN ACID ^a	SAMPLE WEIGHT ^b	WEIGHT LOSS	CORROSION RATE
HRS	GM	GM	MG/SQ IN, HR
0	1.8483		
6.0	1.8466	0.0017	0.37
12.0	1.8448	0.0018	0.39
31.7	1.8390	0.0058	0.39
71.2	1.8271	0.0119	0.39

^a TEMPERATURE OF SOLUTION, 20 °C.

^b AREA OF SAMPLE, 0.763 SQ IN.

TABLE XI

THE CORROSION OF VARIOUS METALS IN HELIUM AND CARBON DIOXIDE ATMOSPHERES
AT TEMPERATURES FROM 593 TO 927 DEGREES CENTIGRADE

TYPE METAL	ATMOSPHERE	TEMPERATURE ^a	EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
		°C			
HASTELLOY B	HELIUM	927	25.33	0.887	4.1
HASTELLOY X	HELIUM	927	25.33	1.016	0.0
347 STAINLESS	HELIUM	927	25.33	0.913	7.1
1020 STEEL	CARBON DIOXIDE	593	6.16	0.811	28.2
1020 STEEL	CARBON DIOXIDE	593	6.16	0.838	20.3
1020 STEEL	CARBON DIOXIDE	593	12.25	0.766	23.4
1020 STEEL	CARBON DIOXIDE	593	12.25	0.838	37.1
1020 STEEL	CARBON DIOXIDE	593	18.00	0.811	49.4
1020 STEEL	CARBON DIOXIDE	593	18.00	0.781	48.8
1020 STEEL	CARBON DIOXIDE	593	25.75	0.868	46.0
1020 STEEL	CARBON DIOXIDE	593	25.75	0.853	23.6
1020 STEEL	CARBON DIOXIDE	677	3.00	0.709	43.4
1020 STEEL	CARBON DIOXIDE	677	6.00	0.823	65.5
1020 STEEL	CARBON DIOXIDE	677	7.84	0.766	132.1
1020 STEEL	CARBON DIOXIDE	677	12.08	0.868	131.1
1020 STEEL	CARBON DIOXIDE	677	13.92	0.823	144.8
1020 STEEL	CARBON DIOXIDE	677	20.00	0.879	134.0
1020 STEEL	CARBON DIOXIDE	843	3.00	0.766	82.2
1020 STEEL	CARBON DIOXIDE	843	6.08	0.897	308.4
1020 STEEL	CARBON DIOXIDE	843	11.92	0.883	659.3
1020 STEEL	CARBON DIOXIDE	843	12.00	0.897	595.2
1020 STEEL	CARBON DIOXIDE	843	18.08	0.897	881.2
1020 STEEL	CARBON DIOXIDE	927	6.16	0.853	612.1
1020 STEEL	CARBON DIOXIDE	927	6.16	0.781	1137.2
1020 STEEL	CARBON DIOXIDE	927	11.84	0.796	1560.3
1020 STEEL	CARBON DIOXIDE	927	11.84	0.751	2084.7
1020 STEEL	CARBON DIOXIDE	927	18.00	0.796	2340.8
1020 STEEL	CARBON DIOXIDE	927	18.00	0.838	2429.6
1020 STEEL	HELIUM	593	6.00	0.941	2.3
1020 STEEL	HELIUM	593	11.92	1.099	8.0
1020 STEEL	HELIUM	593	11.92	1.084	16.2
1020 STEEL	HELIUM	593	18.00	0.941	9.5
1020 STEEL	HELIUM	593	24.00	1.084	28.8
1020 STEEL	HELIUM	593	24.00	0.882	16.9
1020 STEEL	HELIUM	677	12.08	0.926	3.4
1020 STEEL	HELIUM	677	12.08	0.926	3.3
1020 STEEL	HELIUM	677	18.08	0.926	6.4
1020 STEEL	HELIUM	677	24.08	1.027	3.4
1020 STEEL	HELIUM	760	6.00	0.838	6.5
1020 STEEL	HELIUM	760	12.00	0.970	12.8
1020 STEEL	HELIUM	760	12.00	0.868	27.6
1020 STEEL	HELIUM	760	17.92	0.926	46.0
1020 STEEL	HELIUM	760	24.00	0.955	55.2
1020 STEEL	HELIUM	760	24.00	0.883	54.3
1020 STEEL	HELIUM	927	6.08	0.955	9.7
1020 STEEL	HELIUM	927	12.00	0.983	22.3
1020 STEEL	HELIUM	927	12.00	0.955	25.8
1020 STEEL	HELIUM	927	18.00	0.983	31.7
1020 STEEL	HELIUM	927	24.00	0.868	57.7
1020 STEEL	HELIUM	927	30.00	0.883	33.8
1020 STEEL	HELIUM	927	30.00	0.998	50.4
1020 STEEL	HELIUM	927	36.08	0.970	60.7

^a RECORDER-CONTROLLER TEMPERATURE WAS CORRECTED USING FIGURE 8.

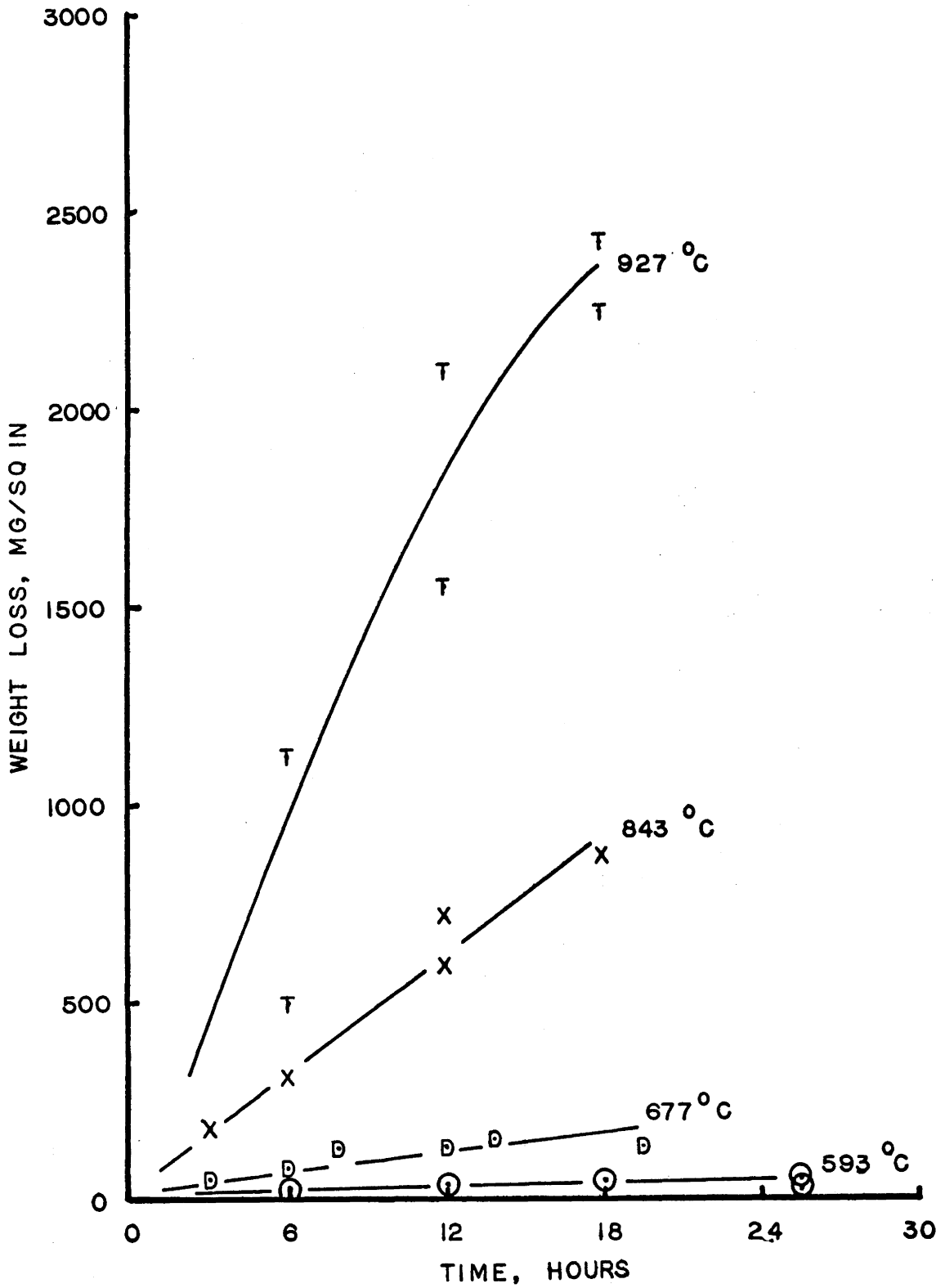


FIGURE 9. EFFECT OF TEMPERATURE ON THE CORROSION OF 1020 CARBON STEEL BY CARBON DIOXIDE

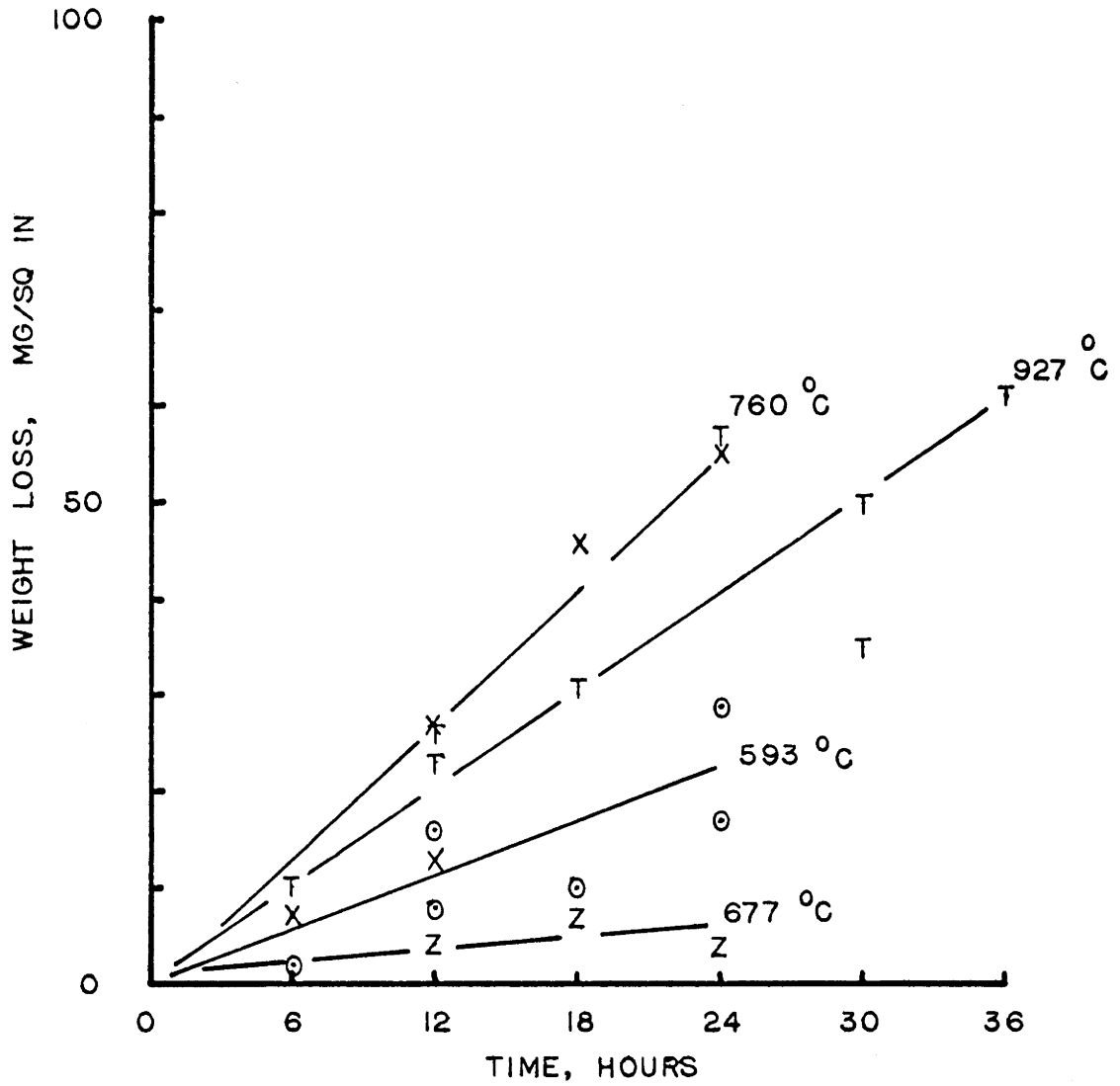


FIGURE 10. EFFECT OF TEMPERATURE ON THE CORROSION OF 1020 CARBON STEEL BY HELIUM

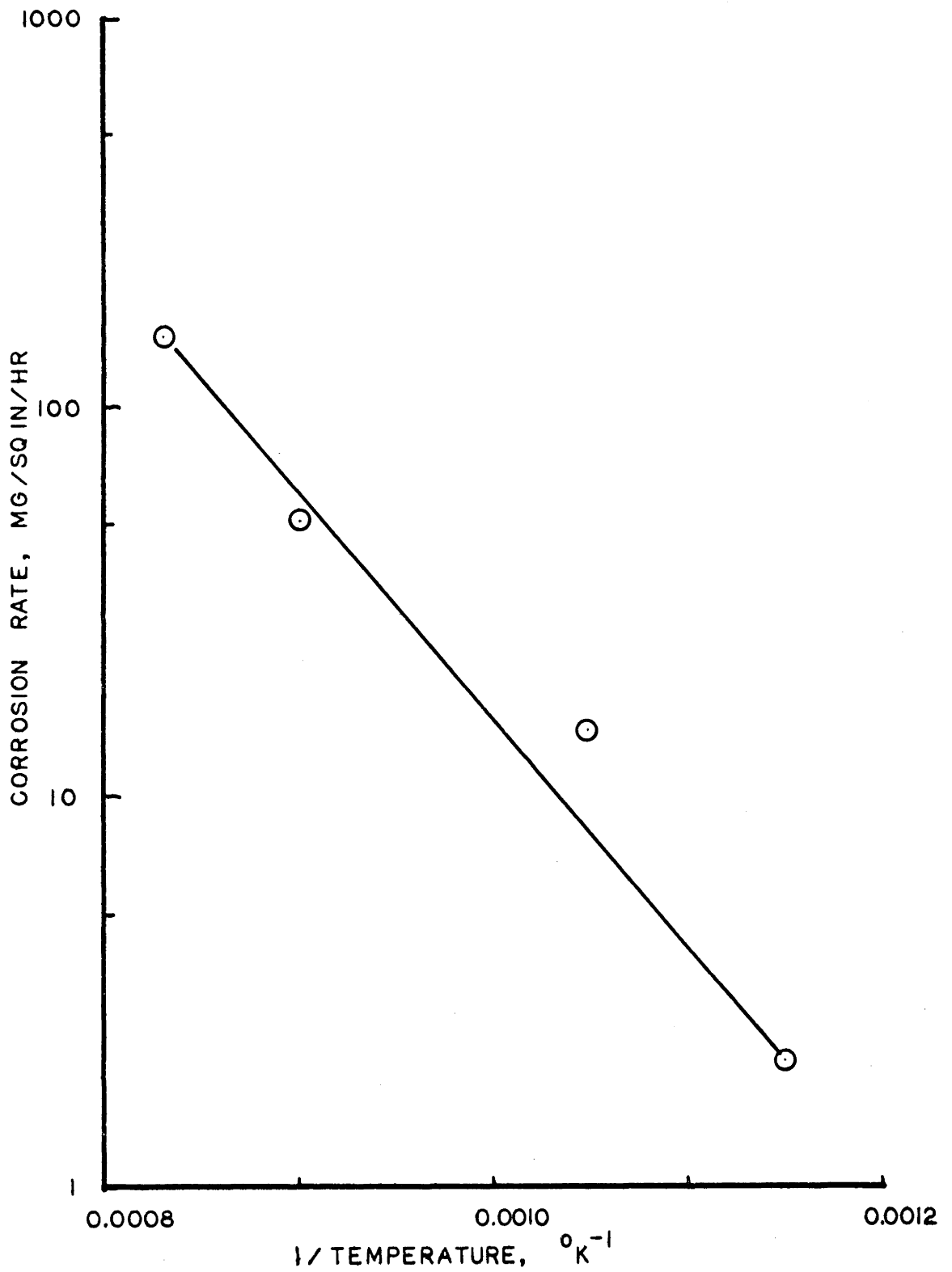


FIGURE 11. ARRHENIUS PLOT FOR THE CORROSION OF 1020 CARBON STEEL BY CARBON DIOXIDE

Effect of Temperature on the Corrosion of 1020 Carbon Steel by Molten Vanadium Pentoxide Slags. To determine the effect of temperature on the corrosion reaction, tests were made at 593 °C, 677 °C, 760 °C, 843 °C, and 927 °C using 1020 carbon steel specimens coated with a 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag. Tests were conducted in both carbon dioxide and helium atmospheres. Data for these tests are given in Table XII and Table XIII. The results are represented graphically in Figures 12 through 21. Arrhenius plots for the data are shown in Figure 22. The corrosion in both carbon dioxide and helium at all temperatures was quite similar, indicating that the atmosphere has little or no effect on the corrosion of the slag coated samples. A very distinct break in the curves which occurs at 677 °C and 760 °C in helium and at 760 °C in carbon dioxide indicates that there are two controlling mechanisms.

Effect of Slag Composition on the Corrosion of 1020 Carbon Steel. To investigate the effect of slag composition on the corrosion of 1020 carbon steel, specimens were coated with sodium carbonate-vanadium

TABLE XII

THE EFFECT OF TEMPERATURE ON THE CORROSION OF 1020 CARBON STEEL IN THE PRESENCE OF A MIXTURE
OF 64 MOLE PER CENT VANADIUM PENTOXIDE AND 36 MOLE PER CENT SODIUM CARBONATE
IN A CARBON DIOXIDE ATMOSPHERE

SPECIMEN TEMPERATURE	EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
°C	HRS	SQ IN	MG/SQ IN
593	6.00	0.767	157.3
593	6.16	0.866	139.0
593	11.50	0.852	132.0
593	11.50	0.877	118.1
593	12.00	0.747	150.9
593	12.00	0.720	137.8
593	18.00	0.761	175.7
593	17.84	0.787	142.9
593	24.00	0.674	141.5
593	30.00	0.746	146.4
593	30.00	0.856	162.5
593	30.33	0.839	145.2
593	36.00	0.765	164.5
677	5.92	0.808	112.2
677	12.00	0.721	128.3
677	12.00	0.781	107.6
677	18.00	0.732	125.0
677	24.00	0.695	121.4
677	30.00	0.739	153.9
677	30.00	0.675	114.5
677	36.00	0.625	148.6
760	6.08	0.782	82.9
760	6.08	0.957	100.7
760	6.08	0.800	113.3
760	12.00	0.761	116.1
760	12.00	0.728	115.5
760	12.25	0.800	124.3
760	18.00	0.808	108.8
760	18.00	0.675	116.9
760	18.00	0.767	129.1
760	24.00	0.793	142.8
760	24.00	0.788	142.5
760	30.00	0.822	155.4
760	30.00	0.800	180.0
760	30.00	0.735	154.4
760	36.00	0.742	208.8
760	36.25	0.765	207.4
843	5.84	0.759	108.1
843	12.42	0.735	157.8
843	12.42	0.703	151.1
843	18.33	0.785	180.3
843	24.00	0.795	183.5
843	30.00	0.940	200.7
843	30.00	0.793	194.8
843	36.50	0.779	191.6
927	6.00	0.862	129.1
927	12.00	0.929	171.1
927	12.00	0.909	167.5
927	18.00	0.909	200.9
927	24.00	0.844	234.5
927	30.00	0.813	277.0
927	30.00	0.882	240.4
927	36.00	0.858	238.9

TABLE XIII

THE EFFECT OF TEMPERATURE ON THE CORROSION OF 1020 CARBON STEEL IN THE PRESENCE OF A MIXTURE
OF 64 MOLE PER CENT VANADIUM PENTOXIDE AND 36 MOLE PER CENT SODIUM CARBONATE
IN A HELIUM ATMOSPHERE

SPECIMEN TEMPERATURE	EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
°C	HRS	SQ IN	MG/SQ IN
593	6.00	0.775	159.4
593	6.16	0.814	120.9
593	12.00	0.708	131.7
593	12.00	0.795	152.1
593	11.50	0.795	129.9
593	11.50	0.802	125.4
593	17.84	0.878	153.6
593	18.00	0.728	102.3
593	24.00	0.742	113.5
593	24.00	0.913	126.9
593	30.00	0.720	126.3
593	30.00	0.740	117.9
593	30.33	0.781	160.2
593	30.33	0.841	141.1
593	35.67	0.864	120.0
593	36.00	0.761	184.1
677	5.92	0.773	125.0
677	12.00	0.681	125.6
677	12.00	0.714	120.6
677	18.08	0.785	130.6
677	24.00	0.767	117.6
677	30.00	0.731	147.7
677	30.00	0.720	155.8
677	36.00	0.806	185.7
760	6.08	0.741	94.5
760	6.08	0.808	90.6
760	6.08	0.966	73.4
760	12.00	0.817	126.7
760	12.08	0.714	115.5
760	12.08	0.754	119.2
760	12.25	0.822	129.1
760	18.00	0.827	134.0
760	18.08	0.779	132.1
760	24.00	0.765	143.8
760	24.00	0.779	130.3
760	30.00	0.822	175.1
760	30.00	0.708	135.3
760	30.00	0.800	179.1
760	36.00	0.795	156.1
760	36.25	0.745	235.5
843	5.83	0.721	118.2
843	12.42	0.727	155.9
843	12.42	0.710	151.7
843	18.33	0.785	169.5
843	24.00	0.826	168.3
843	30.00	0.847	185.6
843	30.00	0.715	168.0
843	36.50	0.779	200.1
927	6.00	0.882	118.5
927	12.00	0.800	158.0
927	12.00	0.875	164.4
927	18.00	0.918	180.3
927	24.00	0.895	197.4
927	30.00	0.895	199.2
927	30.00	0.875	203.3
927	36.00	0.844	210.8

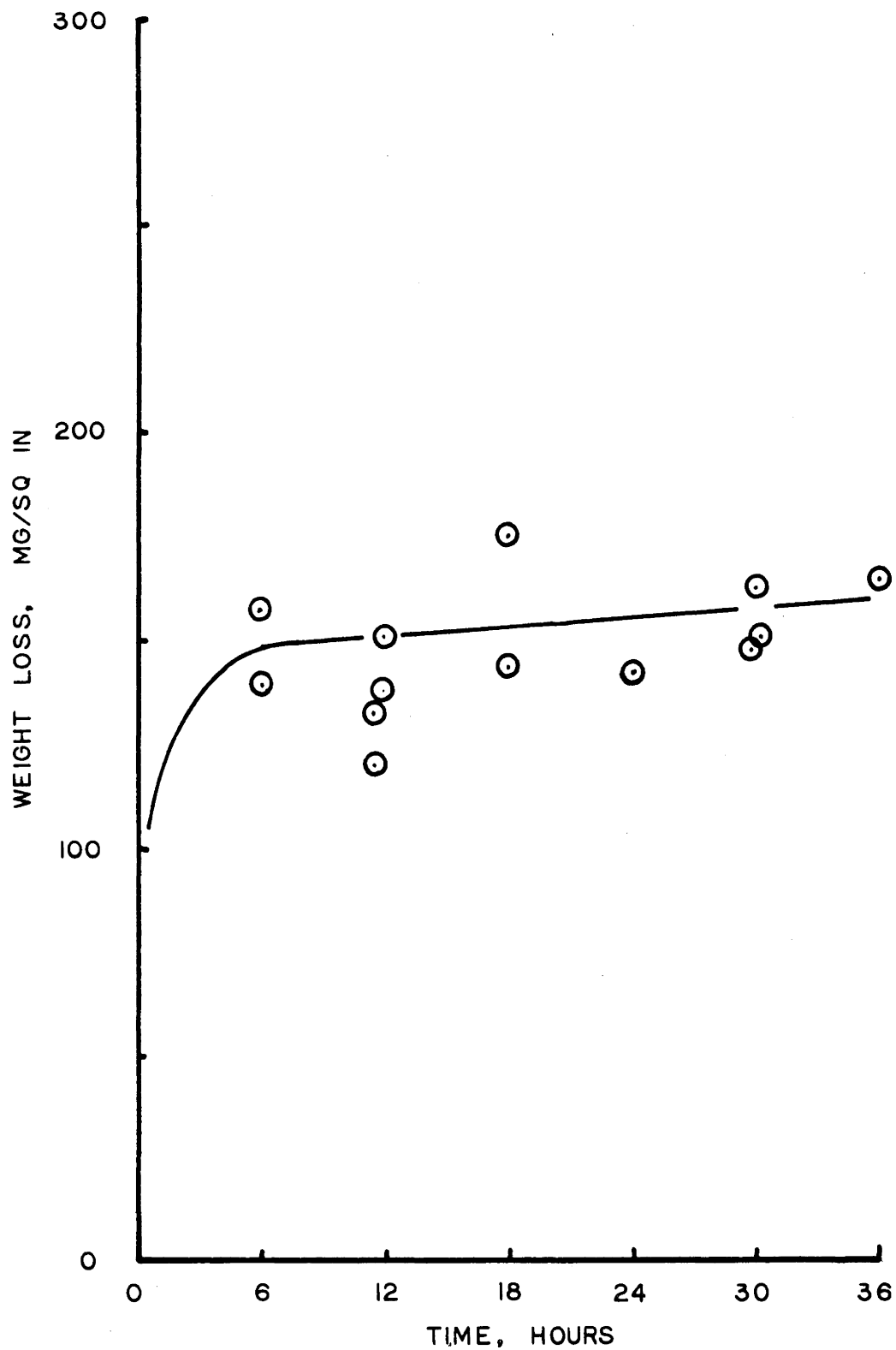


FIGURE 12. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 593 °C IN CARBON DIOXIDE

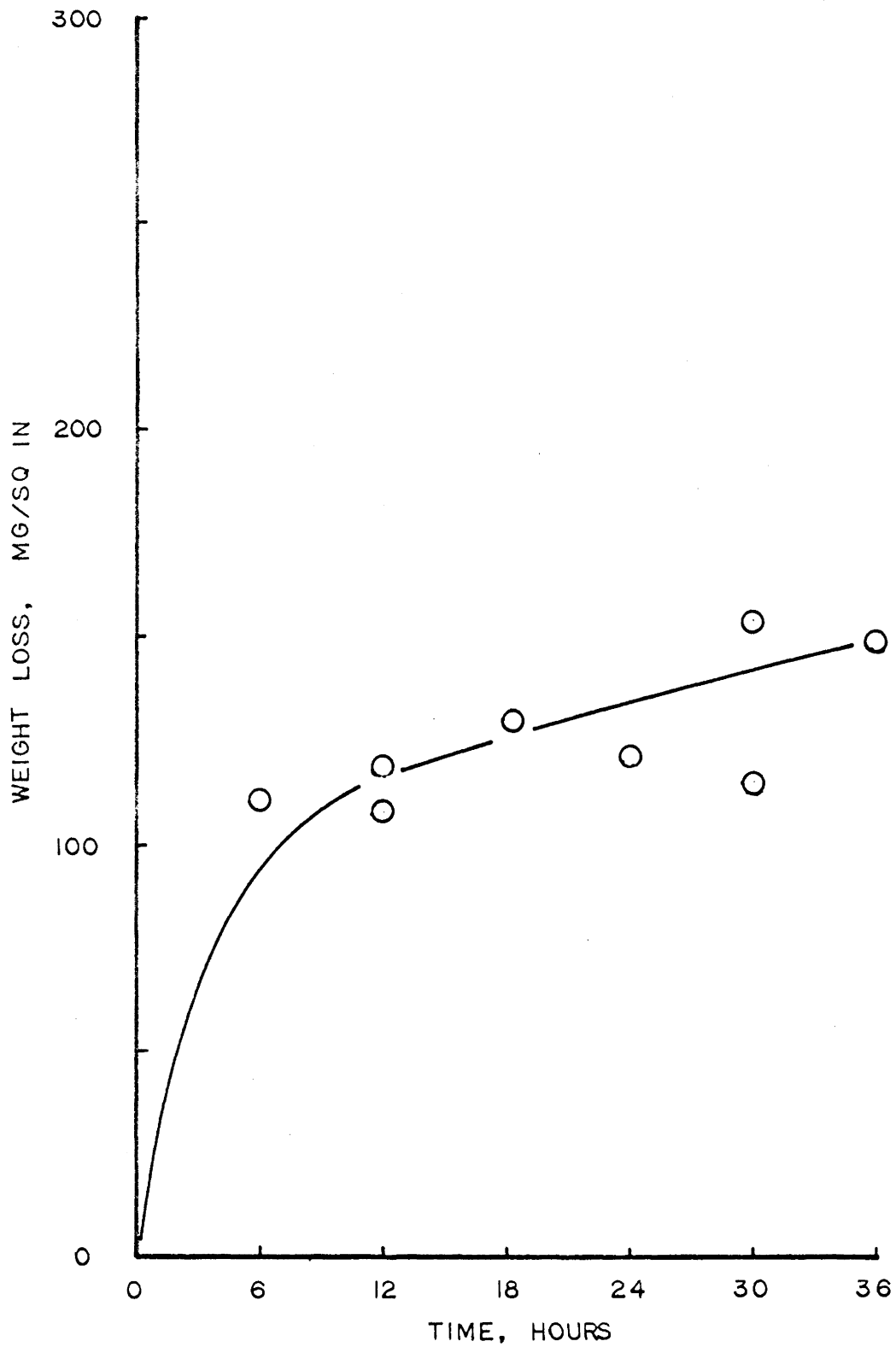


FIGURE 13. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 677 °C IN CARBON DIOXIDE

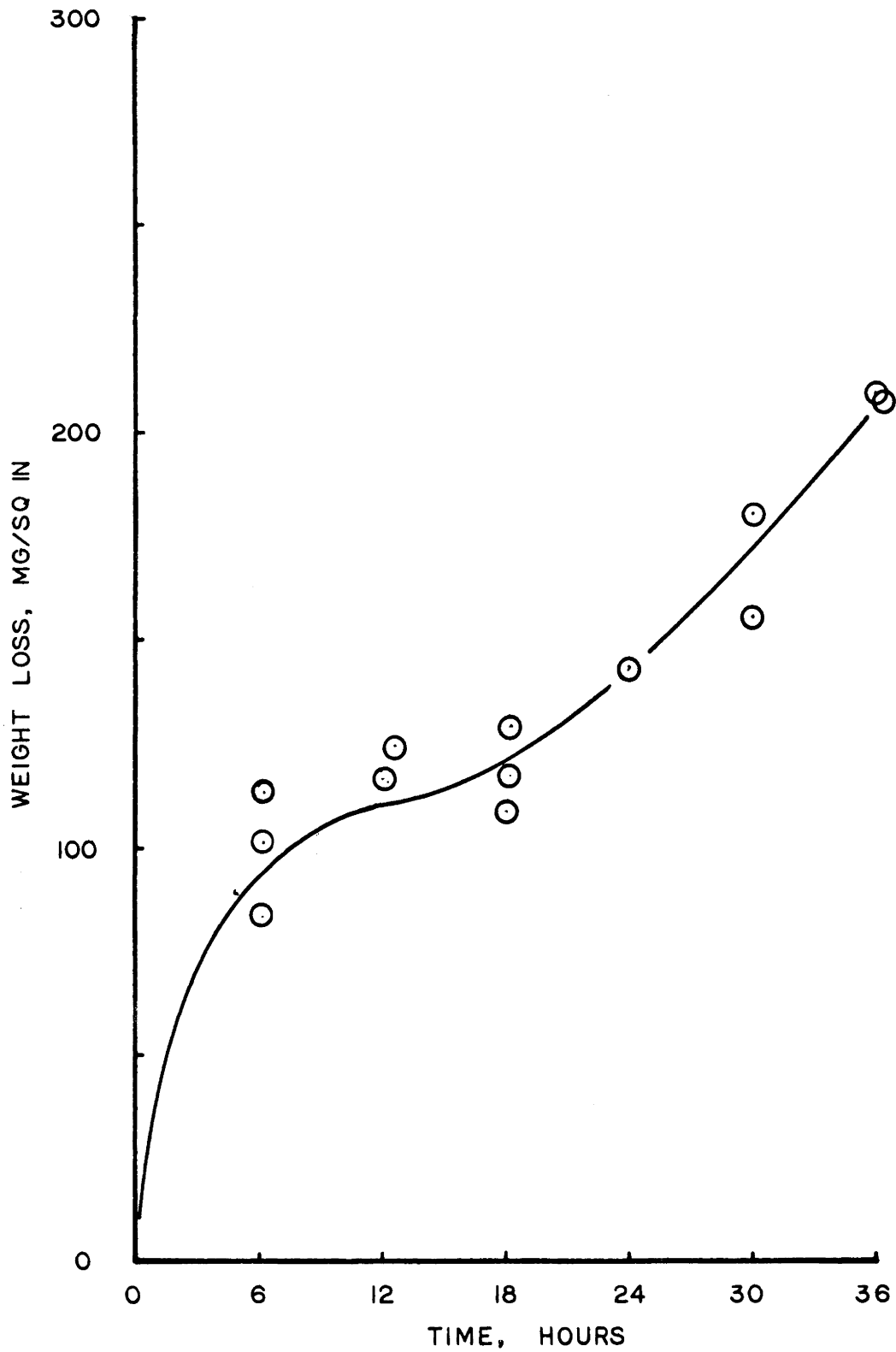


FIGURE 14. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 760 °C IN CARBON DIOXIDE

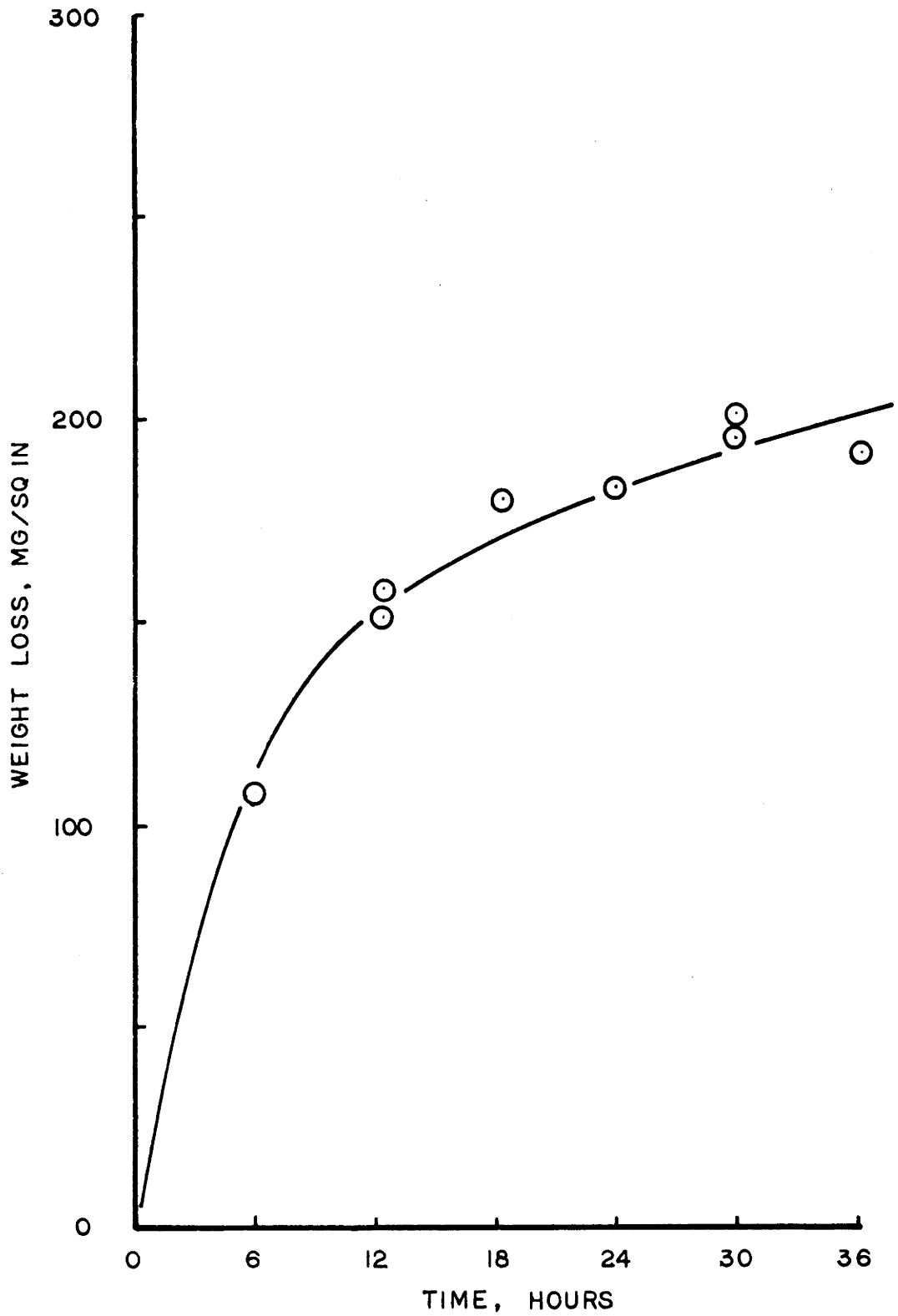


FIGURE 15. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 843 °C IN CARBON DIOXIDE

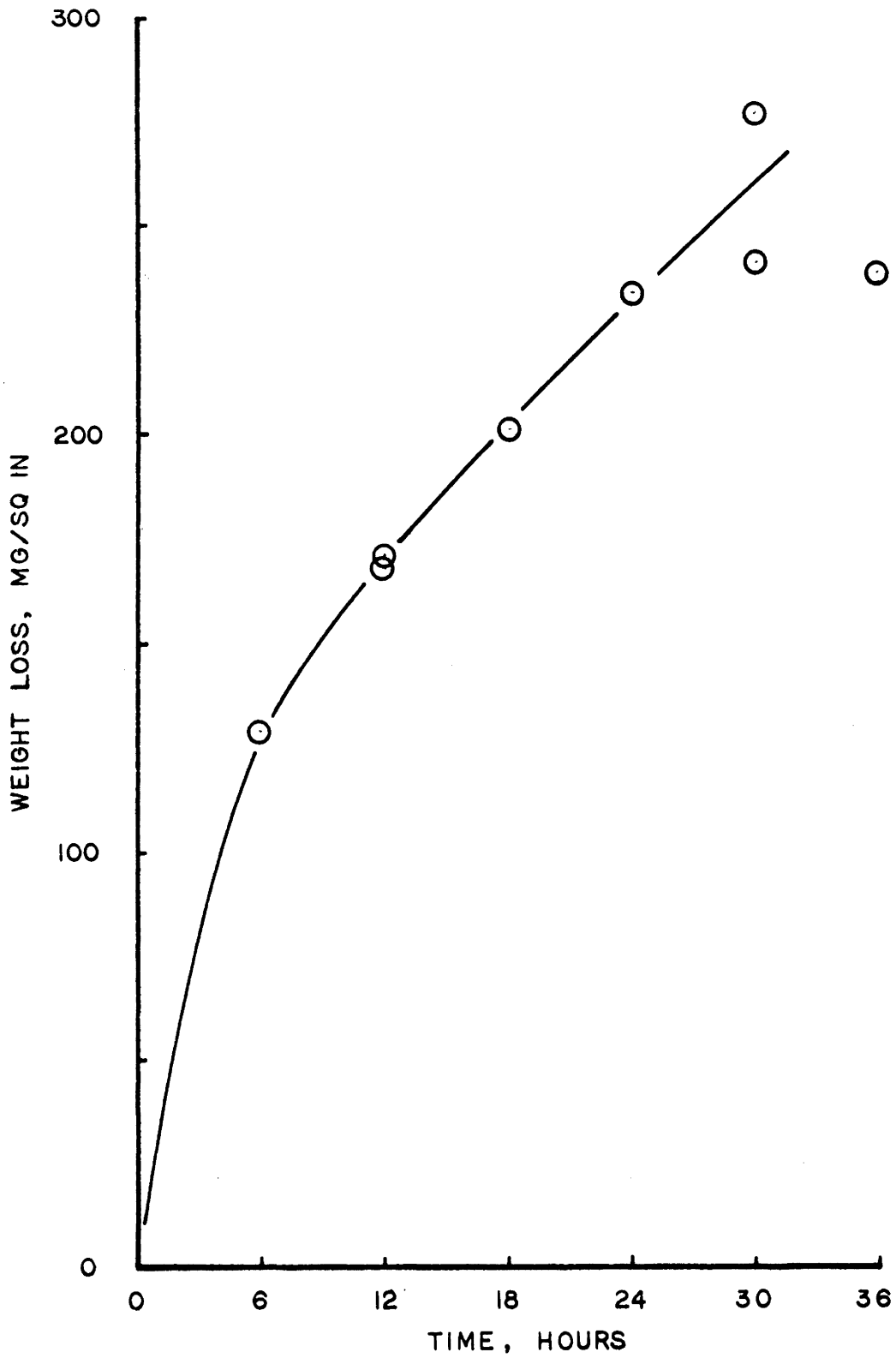


FIGURE 16. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

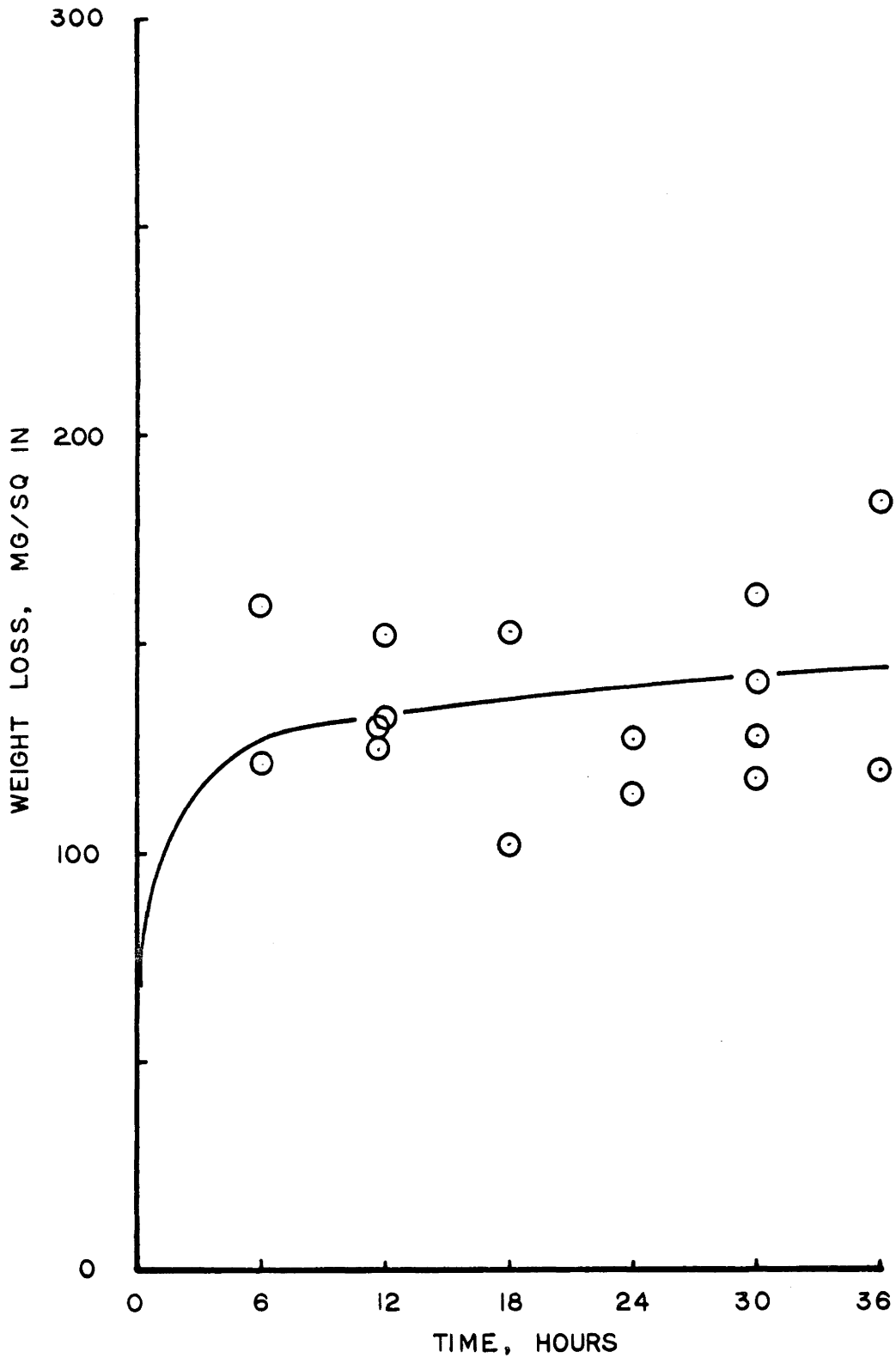


FIGURE 17. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 593 °C IN HELIUM

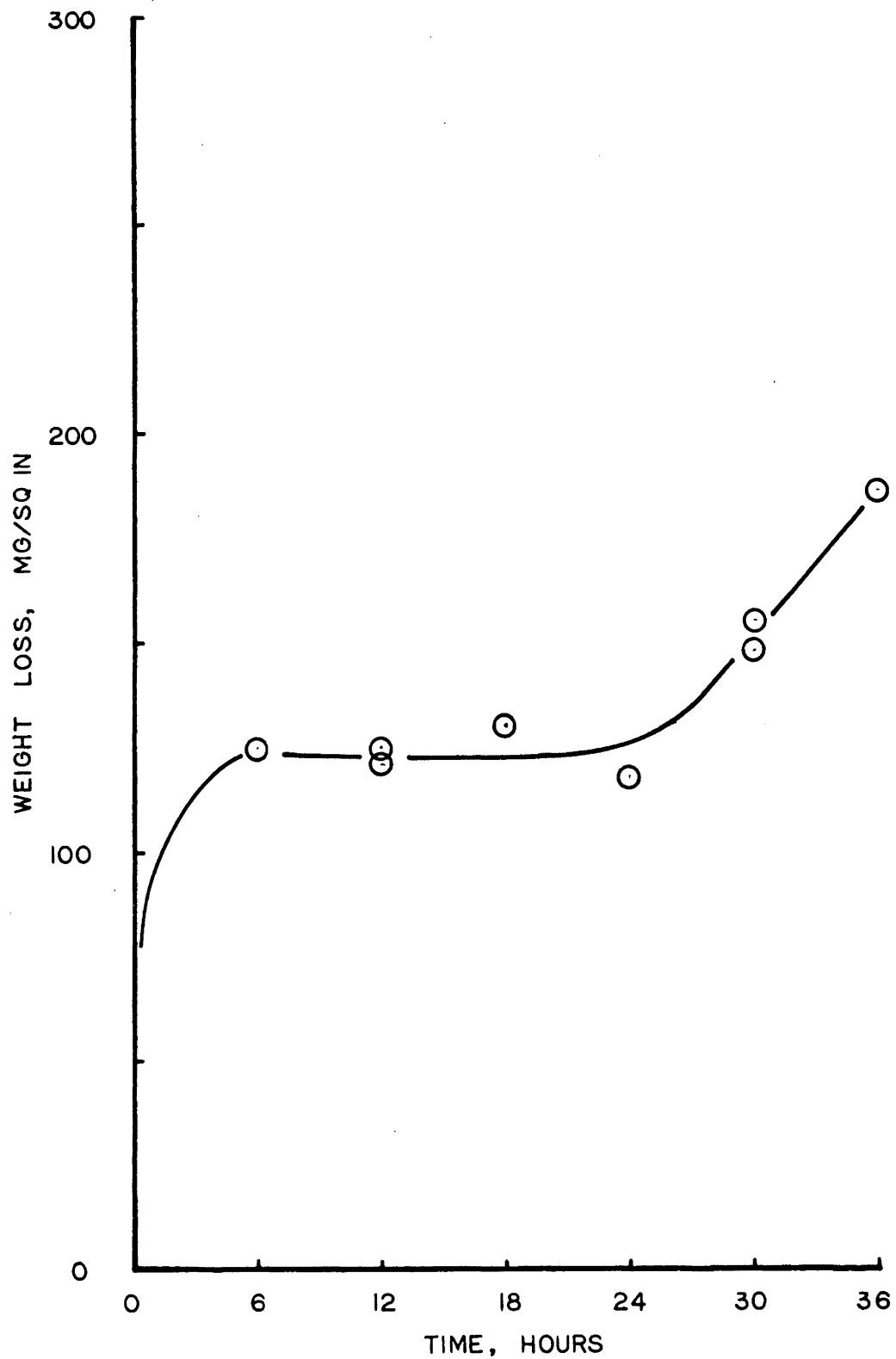


FIGURE 18. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 677 °C IN HELIUM

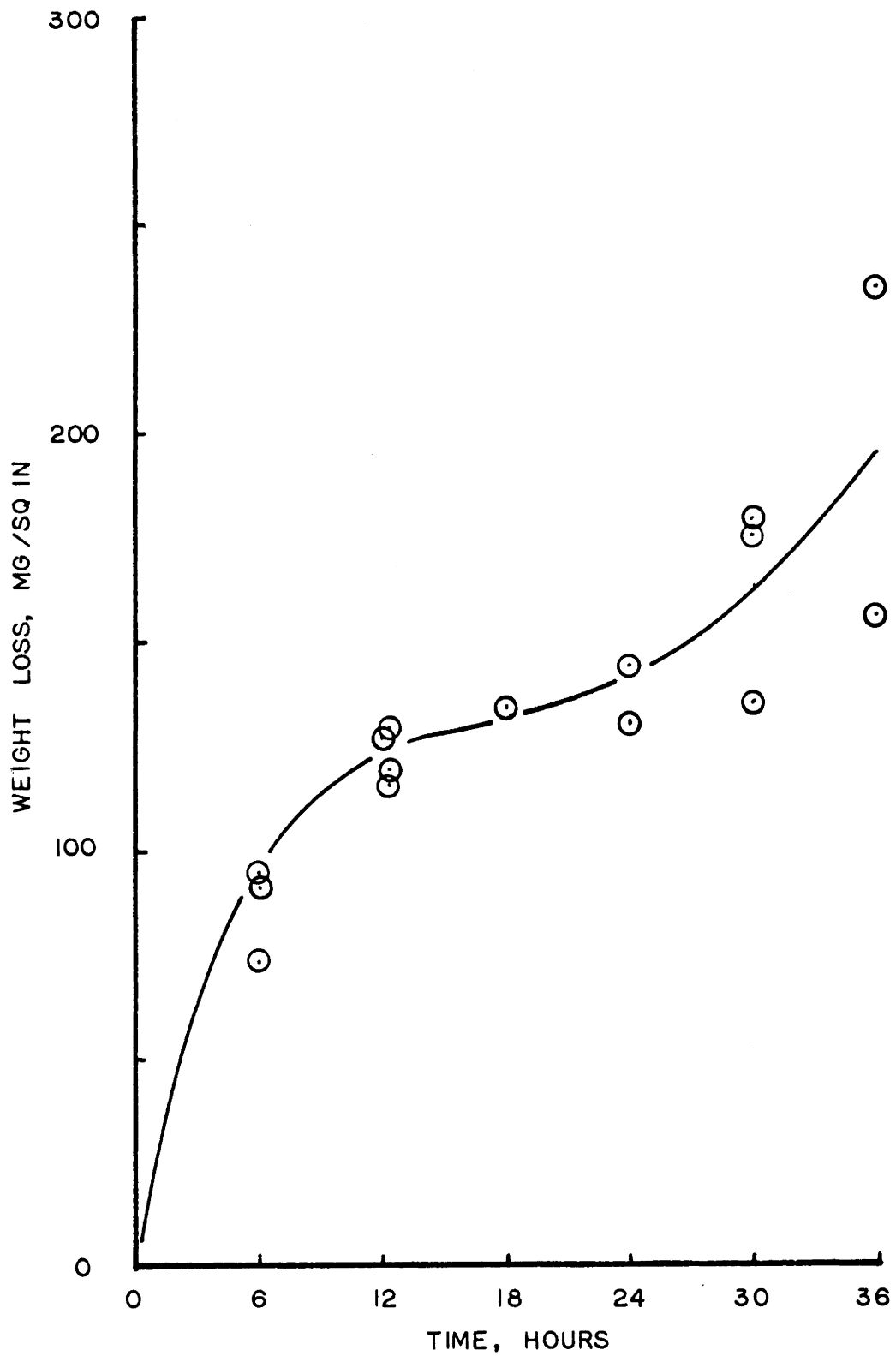


FIGURE 19. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 760 °C IN HELIUM

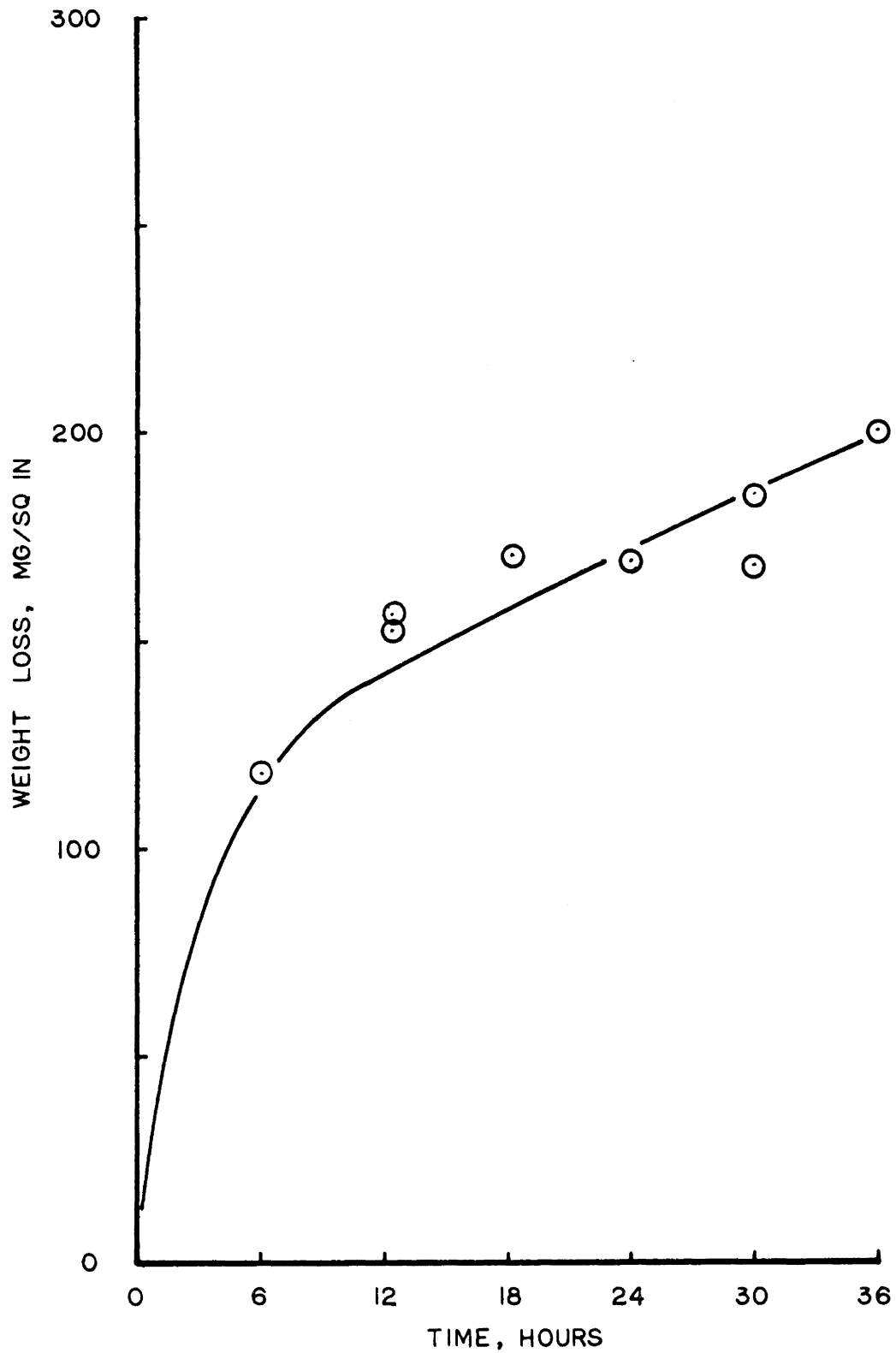


FIGURE 20. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 843 °C IN HELIUM

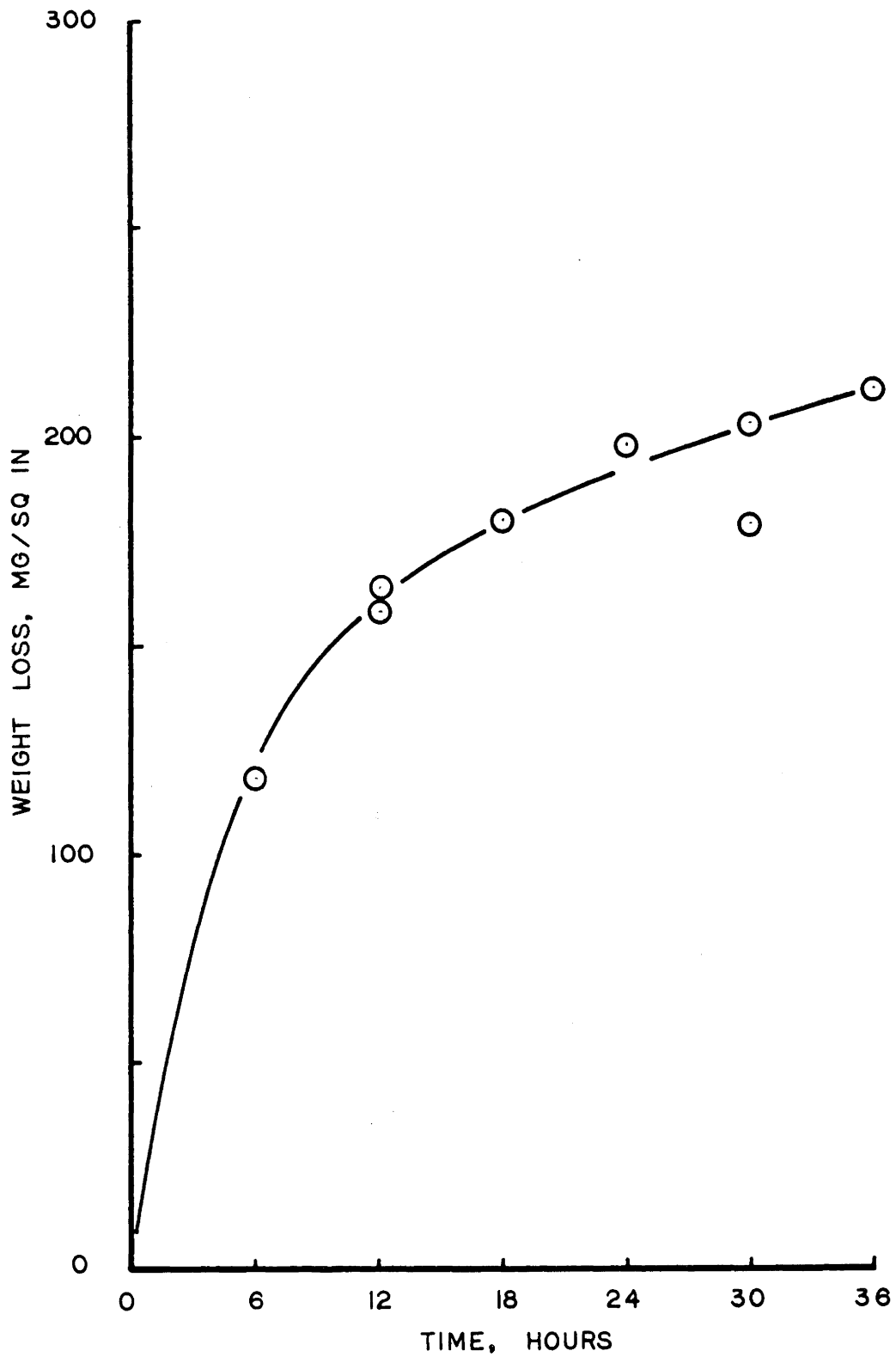


FIGURE 21. THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN HELIUM

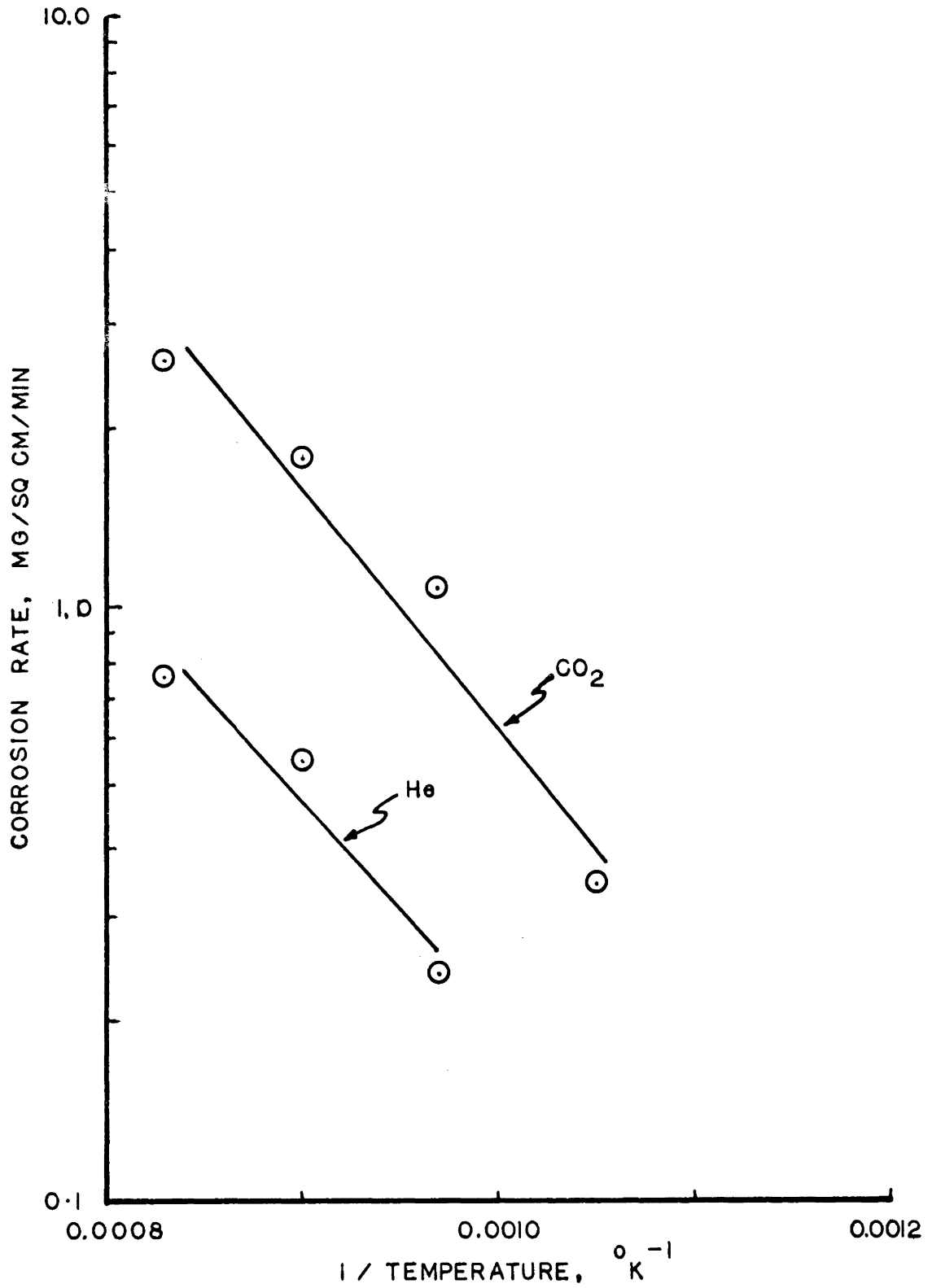


FIGURE 22. ARRHENIUS PLOT FOR THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG IN HELIUM AND CARBON DIOXIDE

pentoxide slags containing 0, 10, 50, 64, and 84 mole per cent vanadium pentoxide. These specimens were heated at 927 °C in both carbon dioxide and helium atmospheres. Data for these tests are given in Table XIV and Table XV. The data are represented graphically in Figures 23 through 30. The initial corrosion rate versus slag composition in both helium and carbon dioxide is plotted in Figure 31. In helium the initial rate of approximately 14 milligrams per square inch, hour, remains constant until the slag composition reaches 50 mole per cent vanadium pentoxide. Above 50 per cent vanadium pentoxide the initial rate increases as the vanadium pentoxide content increases.

Above 50 mole per cent vanadium pentoxide, the initial rates in carbon dioxide are very similar to those in helium, increasing with increasing vanadium pentoxide content.

At zero mole per cent vanadium pentoxide, in both carbon dioxide and helium, the sodium carbonate slags decompose and evaporate from the metal specimens thus exposing the metal surface to the carbon dioxide atmosphere. This phenomenon explains the high

TABLE XIV

THE EFFECT OF SLAG COMPOSITION ON THE CORROSION OF 1020 CARBON STEEL
IN A CARBON DIOXIDE ATMOSPHERE AT 927 DEGREES CENTIGRADE

SLAG COMPOSITION		EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
MOLE % V_2O_5	MOLE % Na_2CO_3	HRS	SQ IN	MG/SQ IN
0	100	6.00	0.793	264.1
0	100	12.25	0.712	585.0
0	100	12.25	0.821	730.7
0	100	17.92	0.767	1076.4
0	100	24.00	0.725	1319.3
0	100	29.67	0.767	1585.8
0	100	29.67	0.735	1402.0
0	100	35.92	0.728	1836.4
10	90	6.00	0.782	778.3
10	90	11.67	0.734	1320.6
10	90	11.67	0.740	1480.3
10	90	18.00	0.829	2025.4
10	90	24.08	0.753	2447.5
10	90	30.42	0.829	2608.9
10	90	30.42	0.829	2556.2
10	90	36.08	0.753	DESTROYED
50	50	6.00	0.767	126.6
50	50	12.75	0.772	179.9
50	50	12.75	0.767	170.7
50	50	18.00	0.747	181.2
50	50	24.00	0.721	244.2
50	50	29.16	0.754	270.0
50	50	29.16	0.740	227.4
50	50	36.00	0.789	248.1
84	16	2.00	0.818	184.2
84	16	2.00	0.852	221.1
84	16	4.08	0.793	245.3
84	16	4.08	0.847	160.6
84	16	6.00	0.740	229.9
84	16	11.92	0.753	230.4
84	16	20.75	0.781	251.1
84	16	24.08	0.781	224.1

TABLE XV

THE EFFECT OF SLAG COMPOSITION ON THE CORROSION OF 1020 CARBON STEEL
IN A HELIUM ATMOSPHERE AT 927 DEGREES CENTIGRADE

SLAG COMPOSITION		EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
MOLE % V_2O_5	MOLE % Na_2CO_3	HRS	SQ IN	MG/SQ IN
0	100	6.08	0.708	64.0
0	100	12.25	0.708	74.8
0	100	12.25	0.752	93.3
0	100	17.92	0.700	130.6
0	100	24.00	0.759	199.9
0	100	29.67	0.816	167.4
0	100	29.67	0.772	203.5
0	100	35.92	0.740	180.6
10	90	6.00	0.752	99.3
10	90	11.67	0.810	167.0
10	90	11.67	0.714	168.9
10	90	18.00	0.773	207.1
10	90	24.08	0.793	210.6
10	90	30.42	0.802	244.8
10	90	30.42	0.801	229.9
10	90	36.08	0.814	252.9
50	50	6.00	0.752	87.9
50	50	12.75	0.779	135.1
50	50	12.75	0.785	134.1
50	50	18.00	0.767	148.8
50	50	24.00	0.801	184.2
50	50	29.25	0.768	198.6
50	50	29.25	0.736	203.2
50	50	36.00	0.681	221.8
84	16	2.00	0.825	210.5
84	16	2.00	0.839	197.0
84	16	4.08	0.765	228.6
84	16	4.08	0.839	189.5
84	16	6.00	0.767	219.0
84	16	11.92	0.754	246.8
84	16	18.75	0.701	224.3
84	16	24.08	0.735	223.8

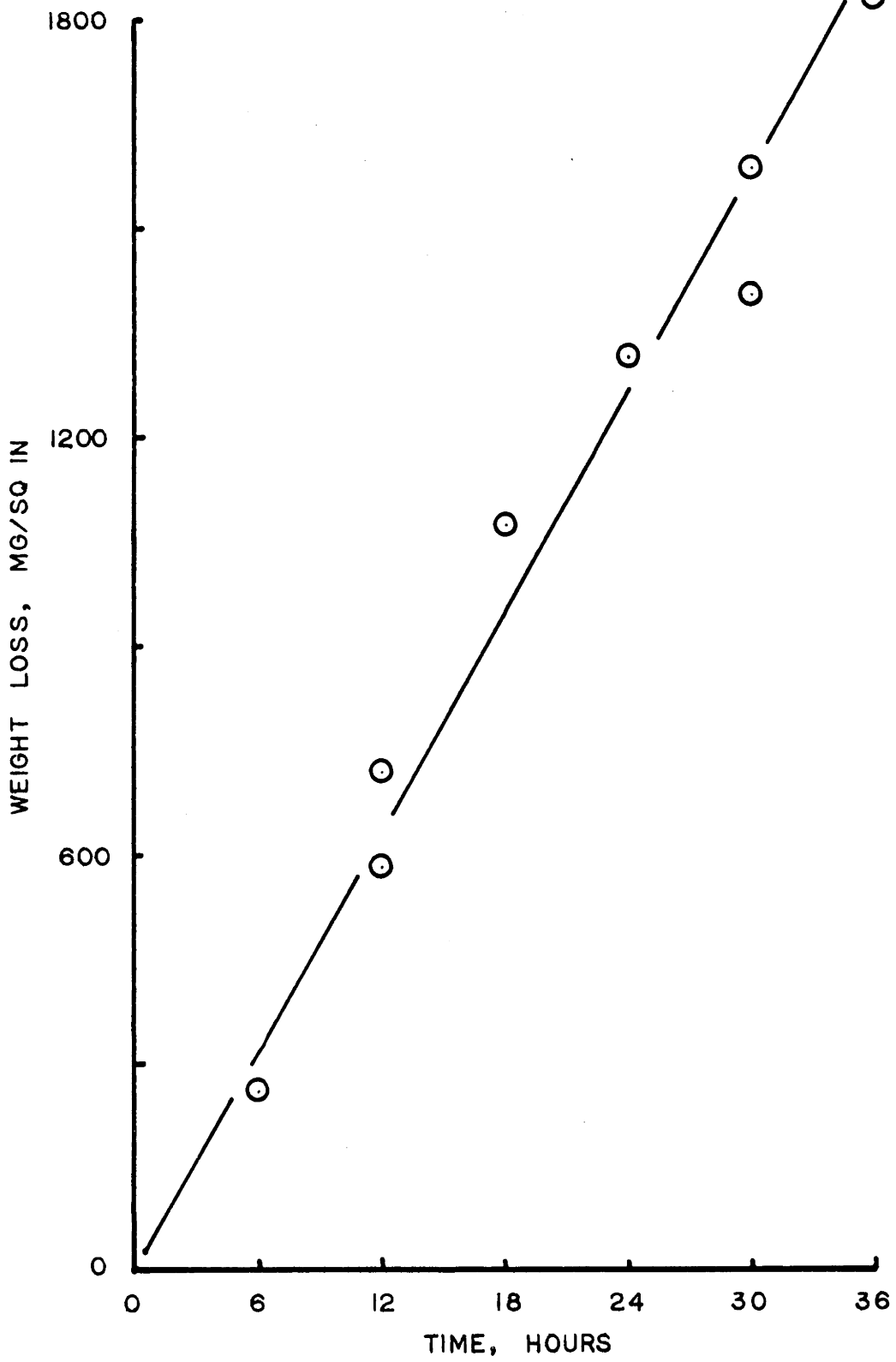


FIGURE 23. THE CORROSION OF 1020 CARBON STEEL BY A SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

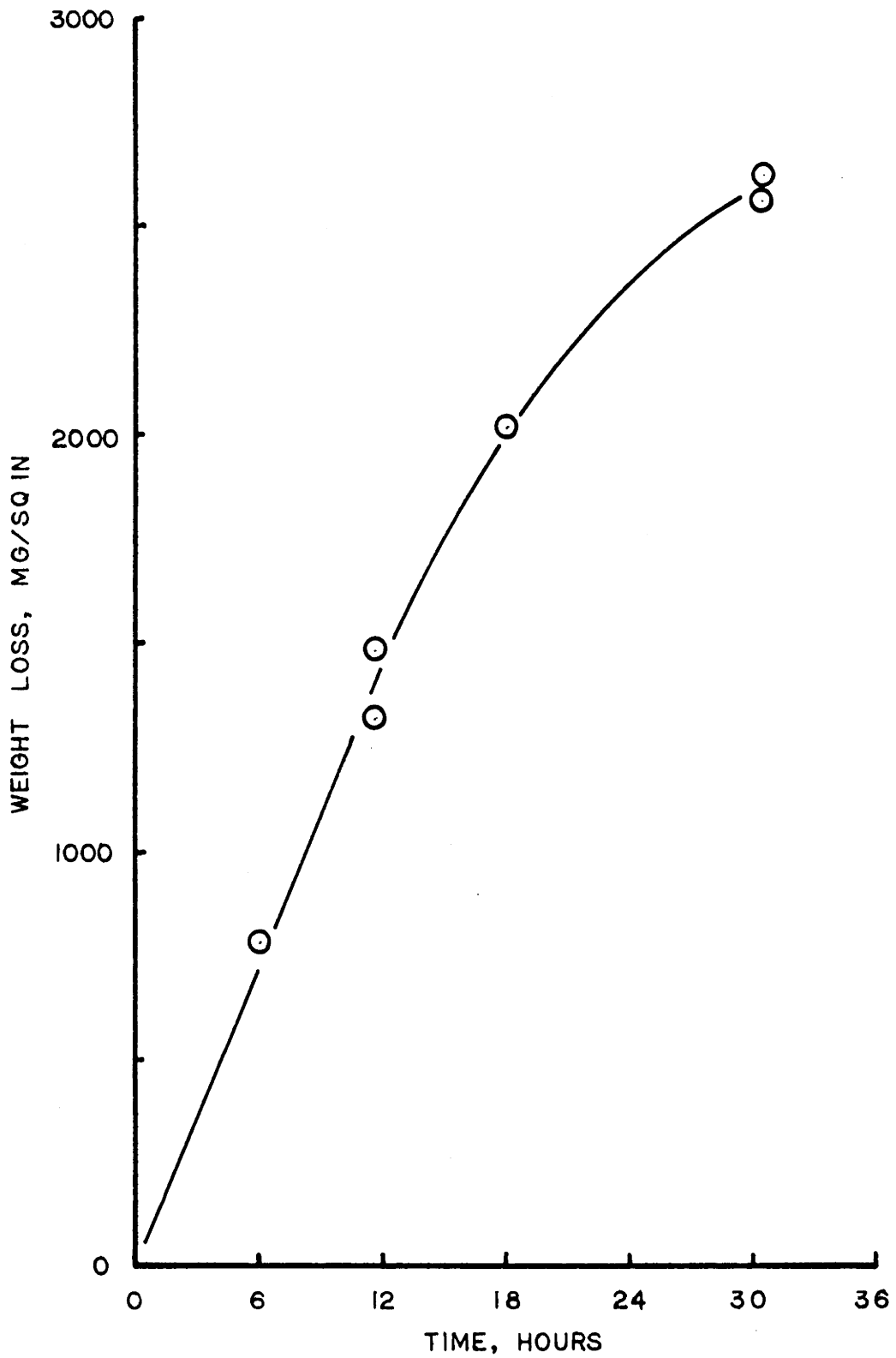


FIGURE 24. THE CORROSION OF 1020 CARBON STEEL BY A 10 MOLE PER CENT VANADIUM PENTOXIDE-90 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

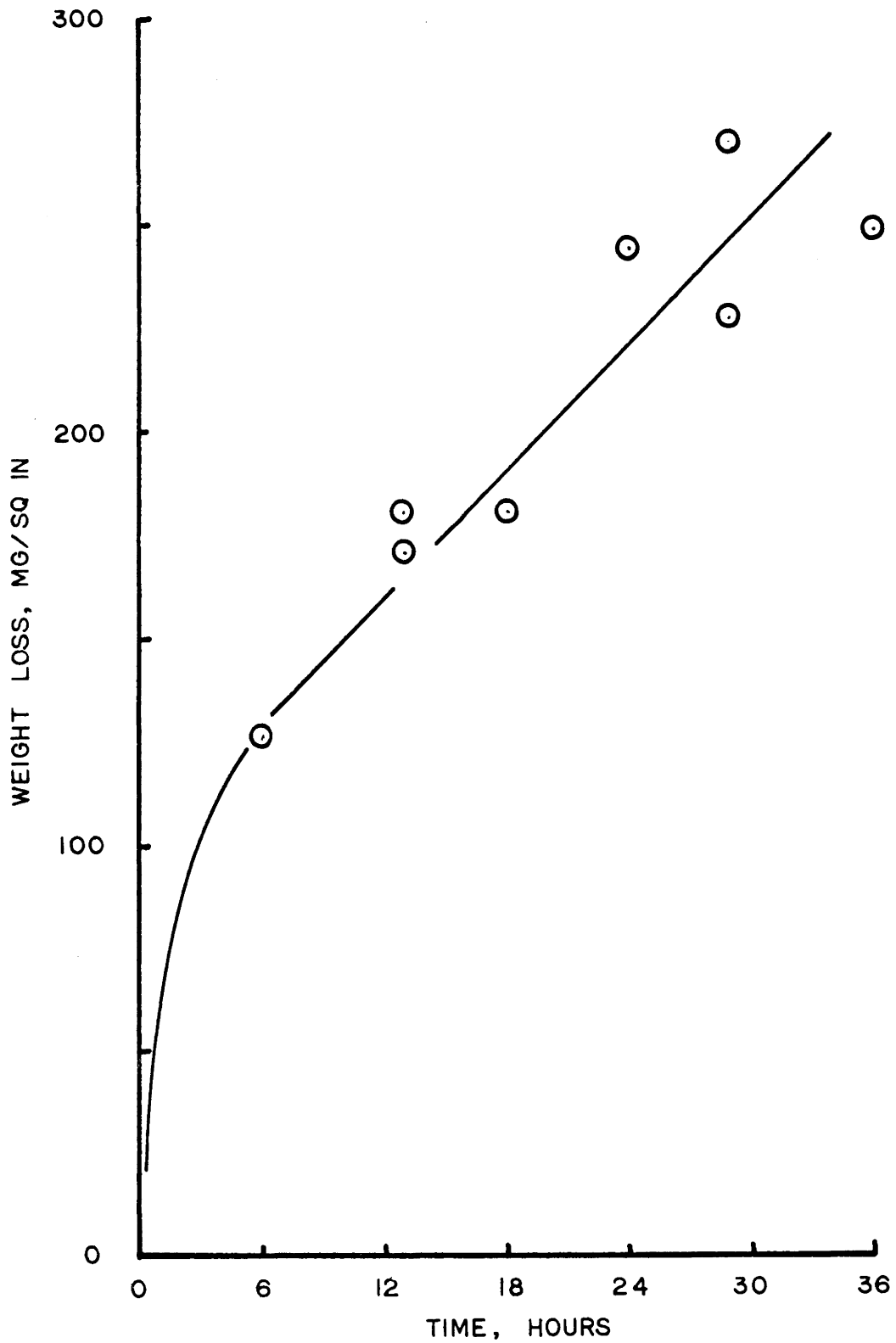


FIGURE 25. THE CORROSION OF 1020 CARBON STEEL BY A 50 MOLE PER CENT VANADIUM PENTOXIDE-50 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

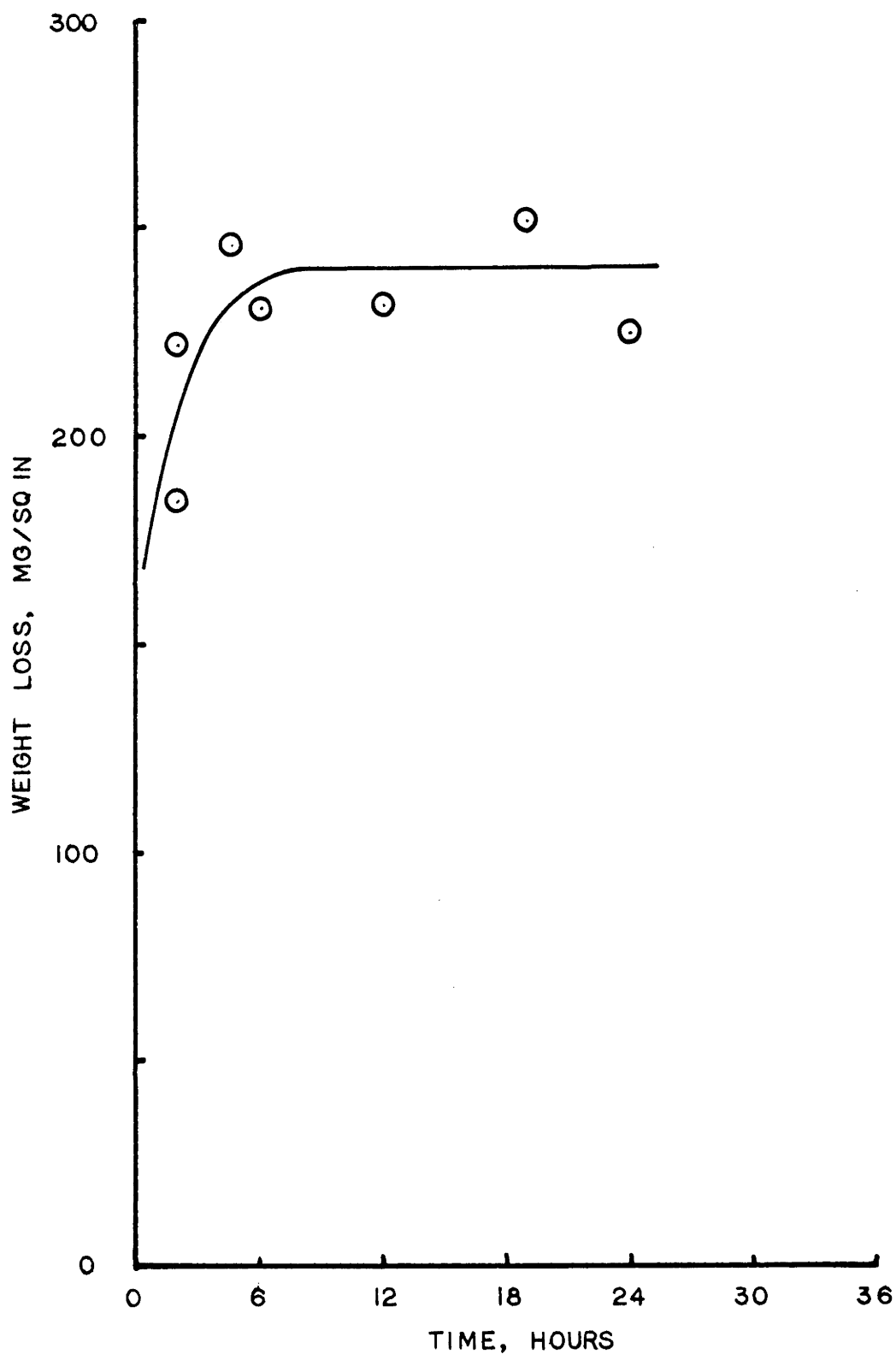


FIGURE 26. THE CORROSION OF 1020 CARBON STEEL BY AN 84 MOLE PER CENT VANADIUM PENTOXIDE-16 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

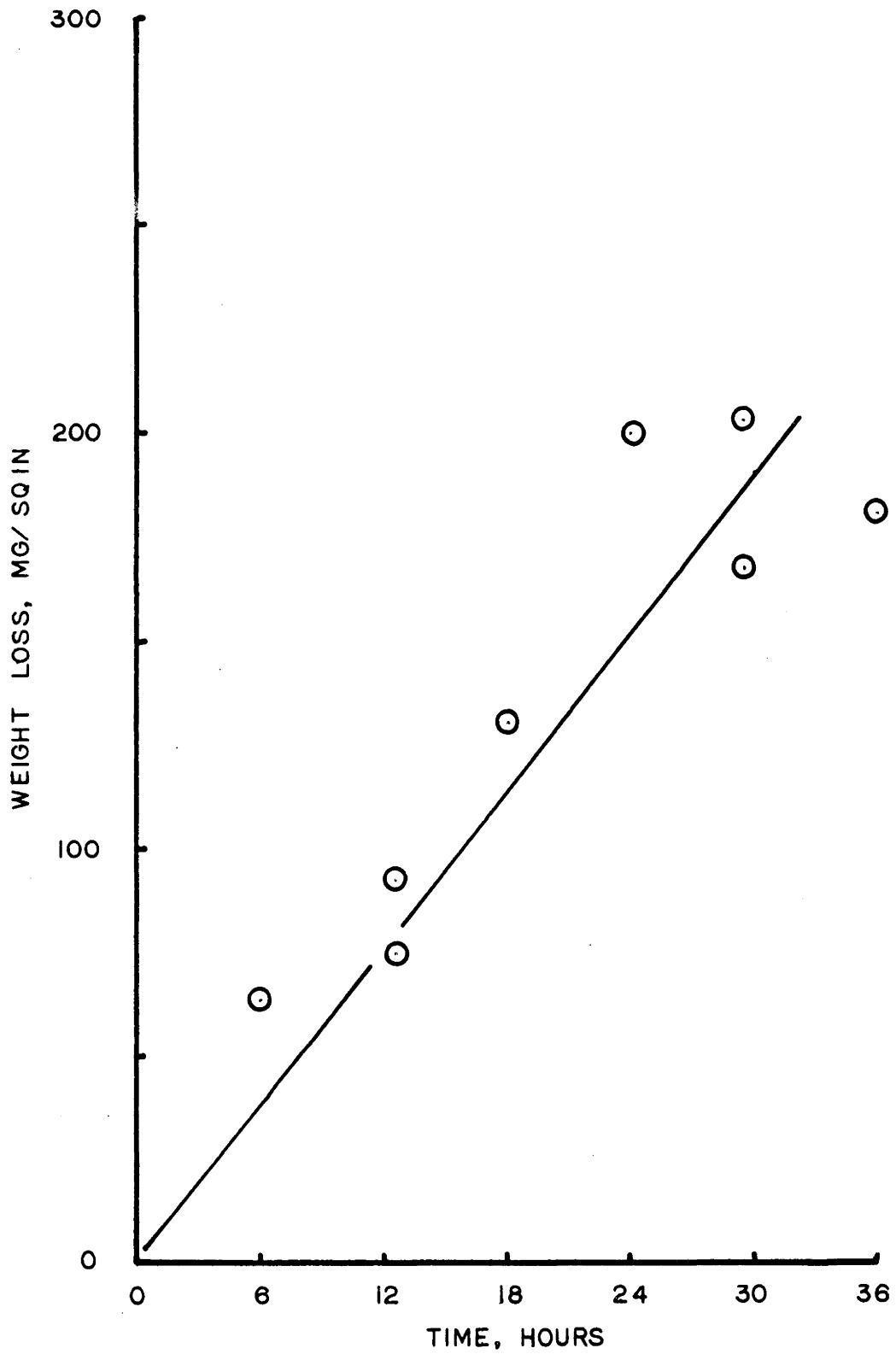


FIGURE 27. THE CORROSION OF 1020 CARBON STEEL BY A SODIUM CARBONATE SLAG AT 927 °C IN HELIUM

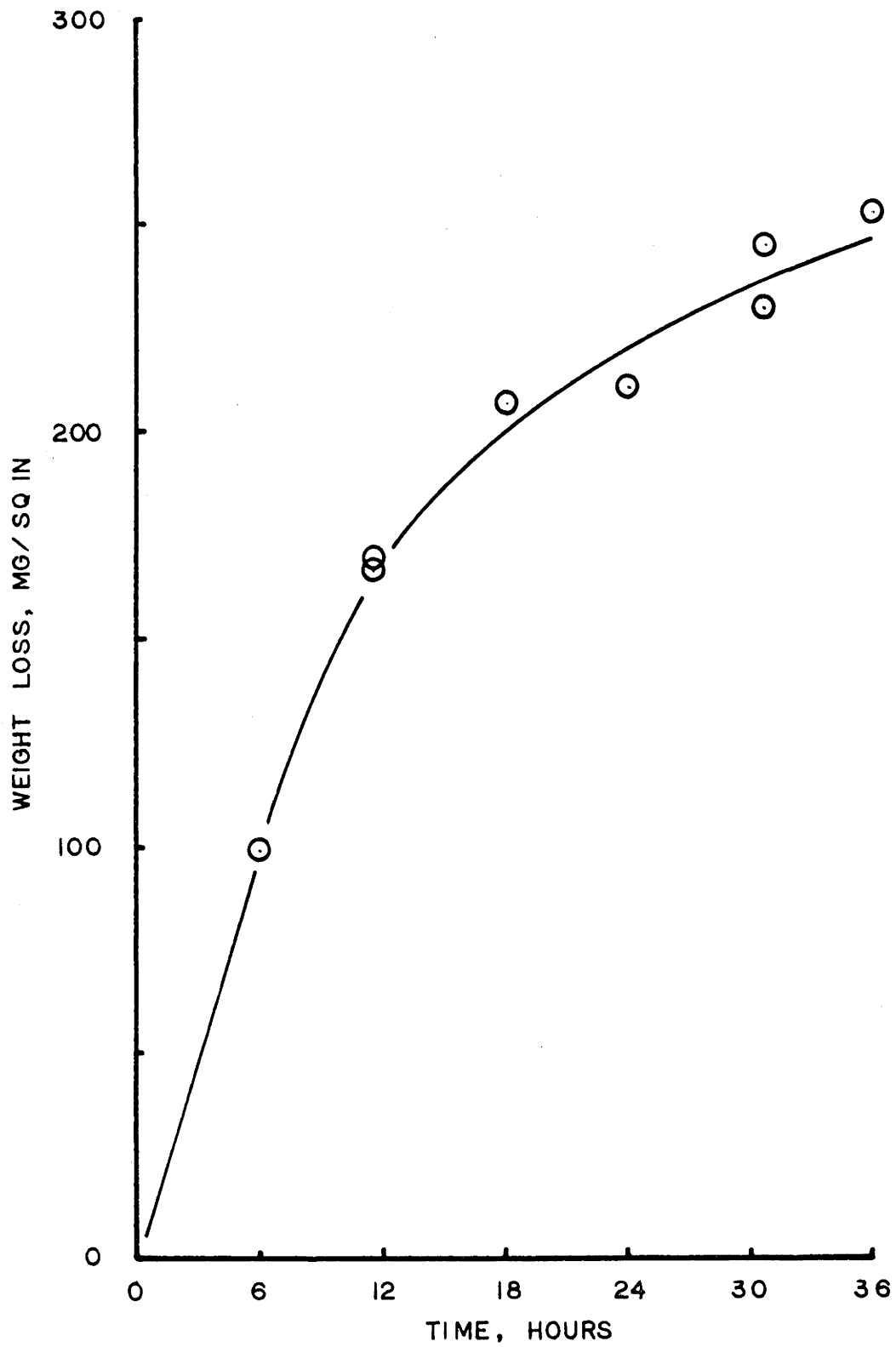


FIGURE 28. THE CORROSION OF 1020 CARBON STEEL BY A 10 MOLE PER CENT VANADIUM PENTOXIDE-90 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN HELIUM

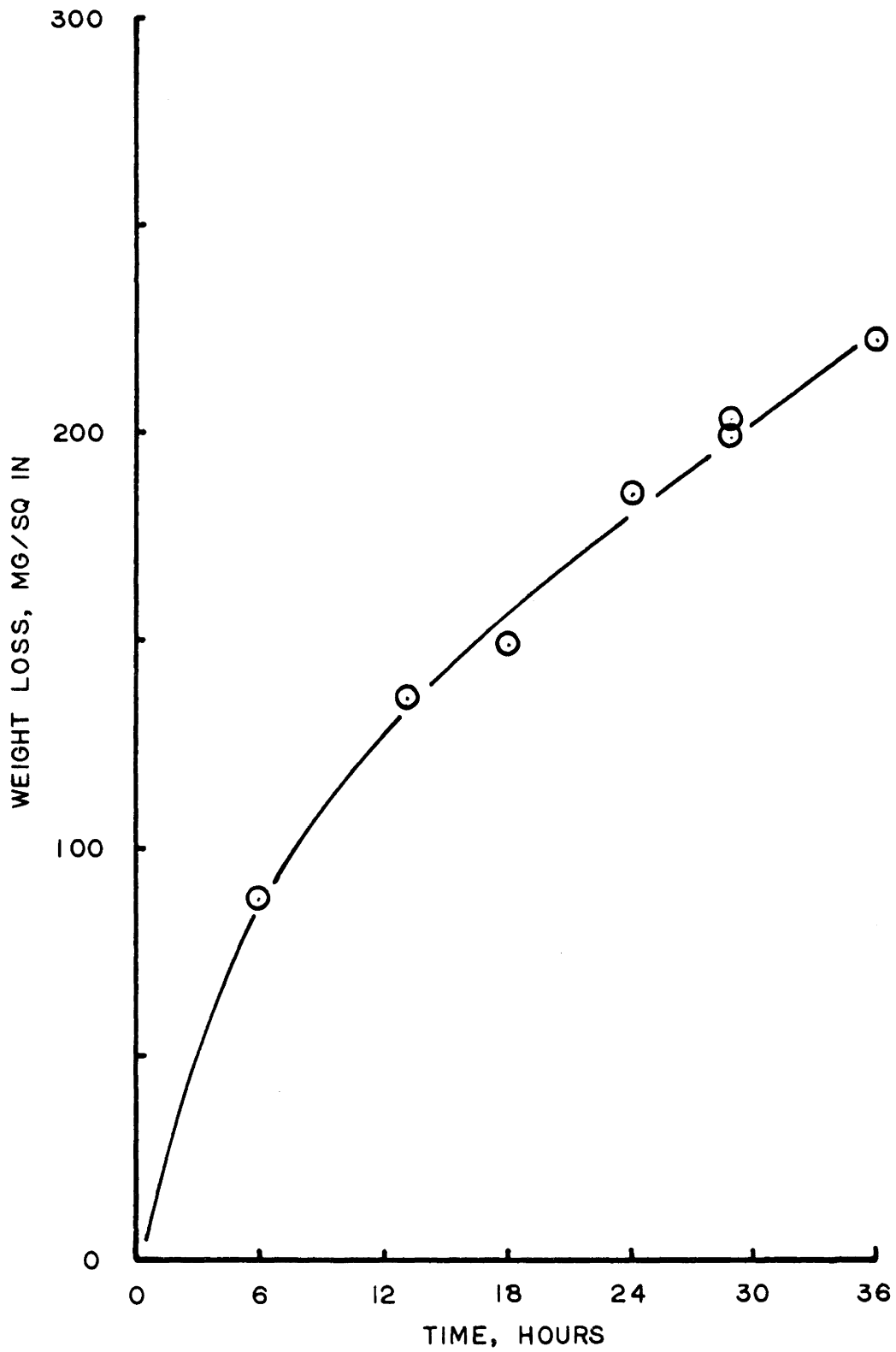


FIGURE 29. THE CORROSION OF 1020 CARBON STEEL BY A 50 MOLE PER CENT VANADIUM PENTOXIDE-50 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN HELIUM

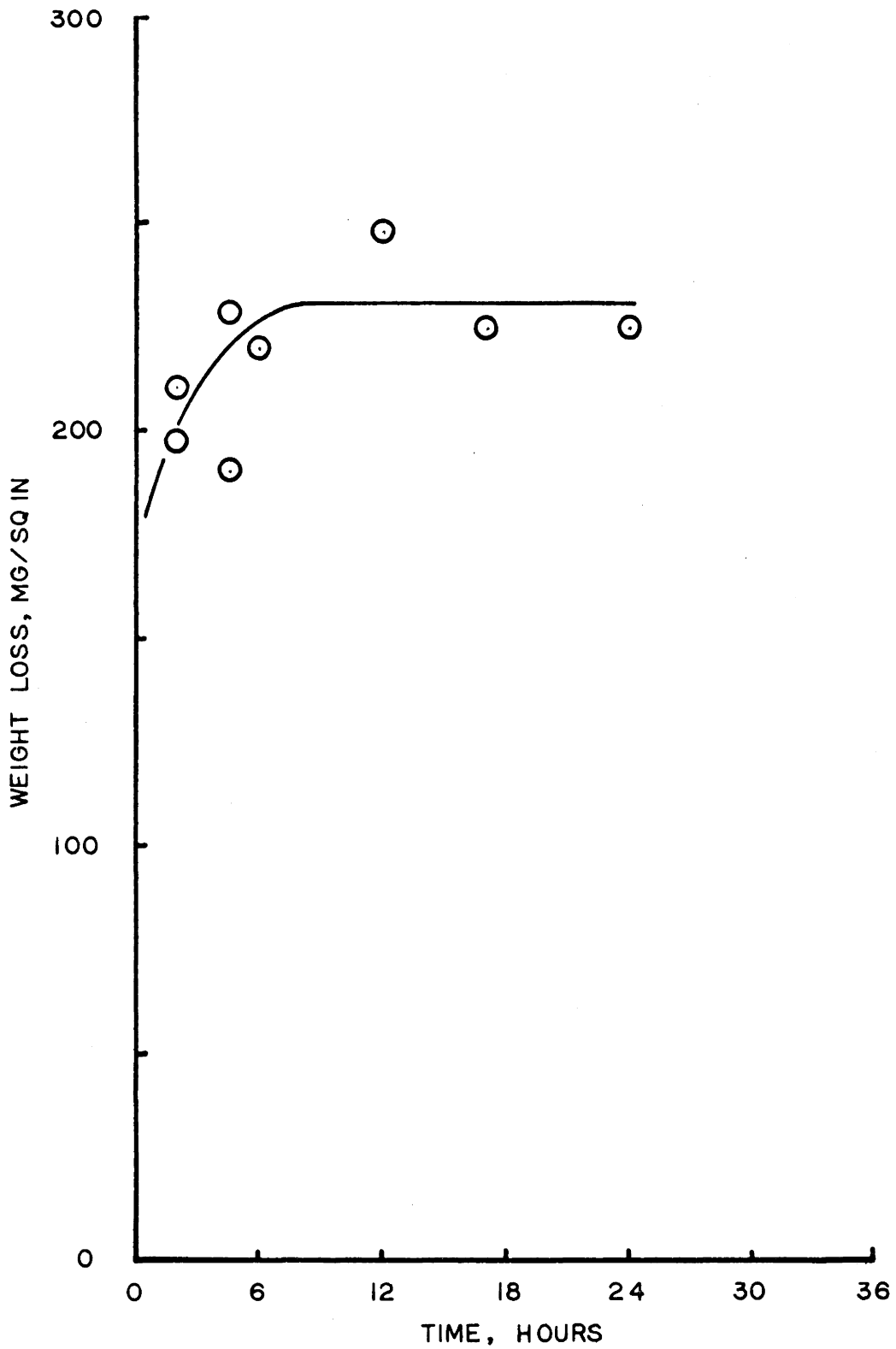


FIGURE 30. THE CORROSION OF 1020 CARBON STEEL BY A 84 MOLE PER CENT VANADIUM PENTOXIDE-16 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN HELIUM

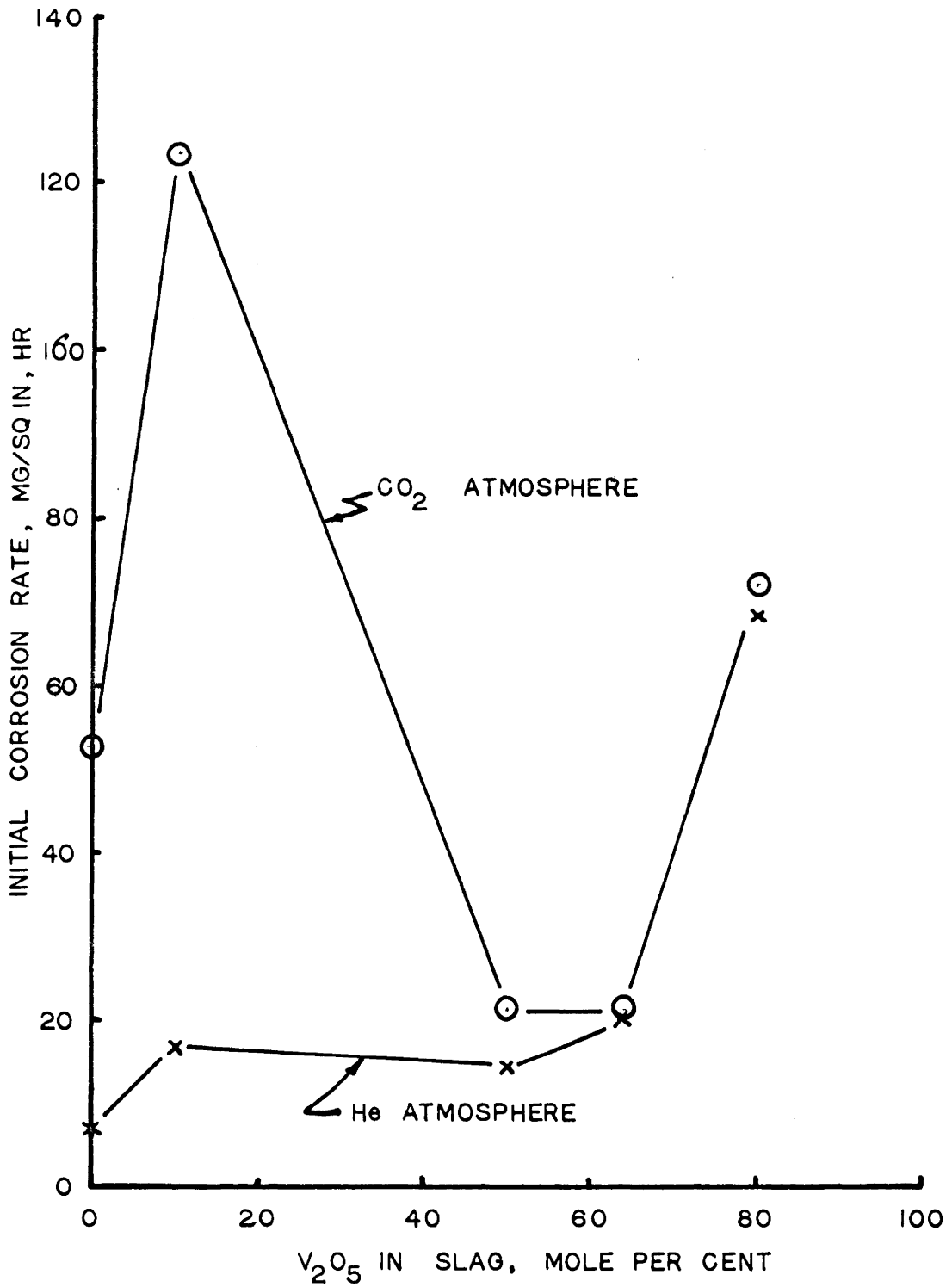


FIGURE 31. EFFECT OF SLAG COMPOSITION ON THE INITIAL CORROSION RATE OF 1020 CARBON STEEL IN CARBON DIOXIDE AT 927 °C

corrosion rate of 1020 carbon steel obtained in carbon dioxide for a slag composed of 100 mole per cent sodium carbonate. The corrosion of 1020 carbon steel in a carbon dioxide atmosphere reached a maximum at a slag composition of 10 mole per cent vanadium pentoxide. Some of this slag also decomposed and evaporated from the metal surface. However, some slag remained for the duration of the test which acted as a flux, removing the products of corrosion from the metal surface, and permitting the attack by carbon dioxide.

Effect of Gas Pressure. To further investigate the effect of carbon dioxide on the corrosion of 1020 carbon steel in the presence of a molten slag containing 64 mole per cent vanadium pentoxide and 36 mole per cent sodium carbonate at 927 °C, tests were made while maintaining carbon dioxide pressures of 15 and 28 pounds per square inch, gage, in the combustion tubes. Data from these tests are shown in Table XVI, and represented graphically in Figure 32.

Effect of Periodic Addition of Fresh Slag. In actual furnace and turbine operation, slag is continuously deposited on the metal surfaces; therefore, tests were conducted in which fresh slag was added to

TABLE XVI

THE EFFECT OF PRESSURE ON THE CORROSION OF 1020 CARBON STEEL
IN THE PRESENCE OF A MIXTURE OF 64 MOLE PER CENT VANADIUM
PENTOXIDE AND 36 MOLE PER CENT SODIUM CARBONATE IN A
CARBON DIOXIDE ATMOSPHERE AT 927 DEGREES CENTIGRADE

PRESSURE	EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
PSIG	HRS	SQ IN	MG/SQ IN
15.0	5.16	0.762	98.4
15.0	12.84	0.818	146.4
15.0	12.84	0.720	153.8
15.0	18.92	0.810	154.6
15.0	24.00	0.773	200.1
15.0	30.00	0.806	232.6
15.0	30.00	0.714	222.6
15.0	37.50	0.767	234.1
28.0	6.00	0.838	104.0
28.0	12.16	0.795	155.8
28.0	12.16	0.702	166.5
28.0	18.16	0.844	180.8
28.0	24.00	0.801	227.4
28.0	30.00	0.785	269.4
28.0	30.00	0.808	245.4
28.0	36.16	0.708	239.1

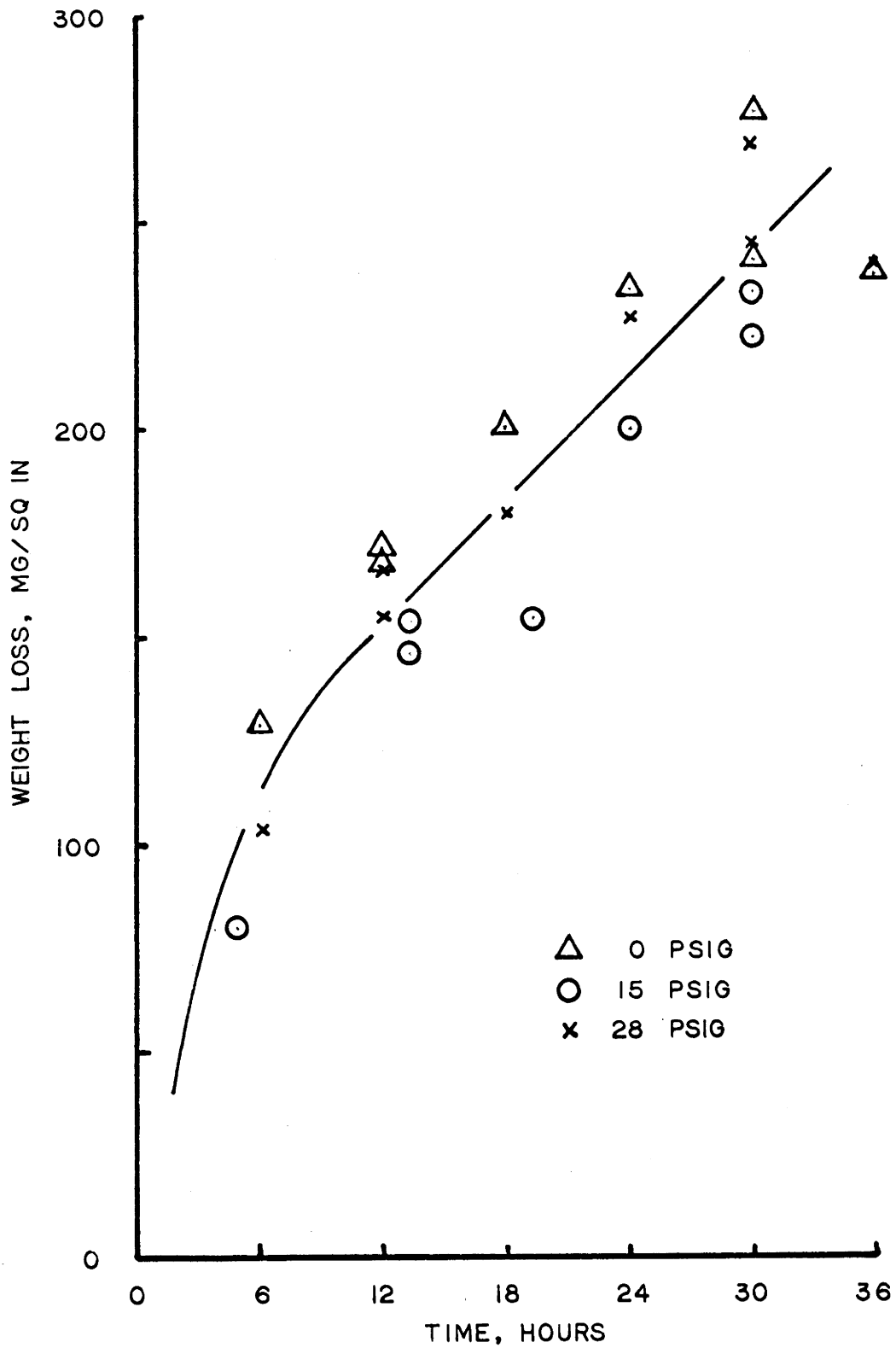


FIGURE 32. THE EFFECT OF PRESSURE ON THE CORROSION OF 1020 CARBON STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

the corroding specimens periodically. These tests were made using 1020 carbon steel specimens, a slag containing 84 mole per cent vanadium pentoxide, a carbon dioxide atmosphere, and a temperature of 927 °C. Results of these tests are shown in Table XVII and Figure 33. It is interesting to note that in these tests the corrosion reaction continues rather than leveling off after a weight loss of 240 milligrams per square inch, as observed for tests conducted in the standard manner, Figure 26, page 84, indicating that a component of the slag and not the atmosphere is the major cause of corrosion.

Corrosion of Alloys by Molten Slags Containing Vanadium Pentoxide. Tests were made to determine the corrosion of Hastelloy B, Hastelloy X, and 347 stainless steel by a molten slag containing 64 mole per cent vanadium pentoxide and 36 mole per cent sodium carbonate in a carbon dioxide atmosphere. Data and results from these tests are shown in Table XVIII and Figures 34 through 37. The relative corrosion of the three alloys at 927 °C is shown in Figure 37; as the nickel content of the alloy increases, the corrosion rate increases. Hastelloy B, with nickel content of

TABLE XVII

THE EFFECT OF PERIODIC SLAG ADDITION ON THE CORROSION OF 1020 CARBON
STEEL BY AN 84 MOLE PER CENT VANADIUM PENTOXIDE-16 MOLE PER CENT
SODIUM CARBONATE SLAG AT 927 DEGREES CENTIGRADE
IN CARBON DIOXIDE

EXPOSURE TIME ^a	SAMPLE AREA	CORRECTED WEIGHT LOSS
HRS	SQ IN	MG/SQ IN
0.00	0.809	2.5
5.00	0.829	203.5
10.08	0.878	377.5
17.50	0.806	513.5

^a ALL SAMPLES WERE REDIPPED IN THE SLAG EACH TIME THE FURNACE WAS OPENED TO REMOVE A SAMPLE. THE SAMPLES WERE NOT CLEANED BEFORE THEY WERE REDIPPED.

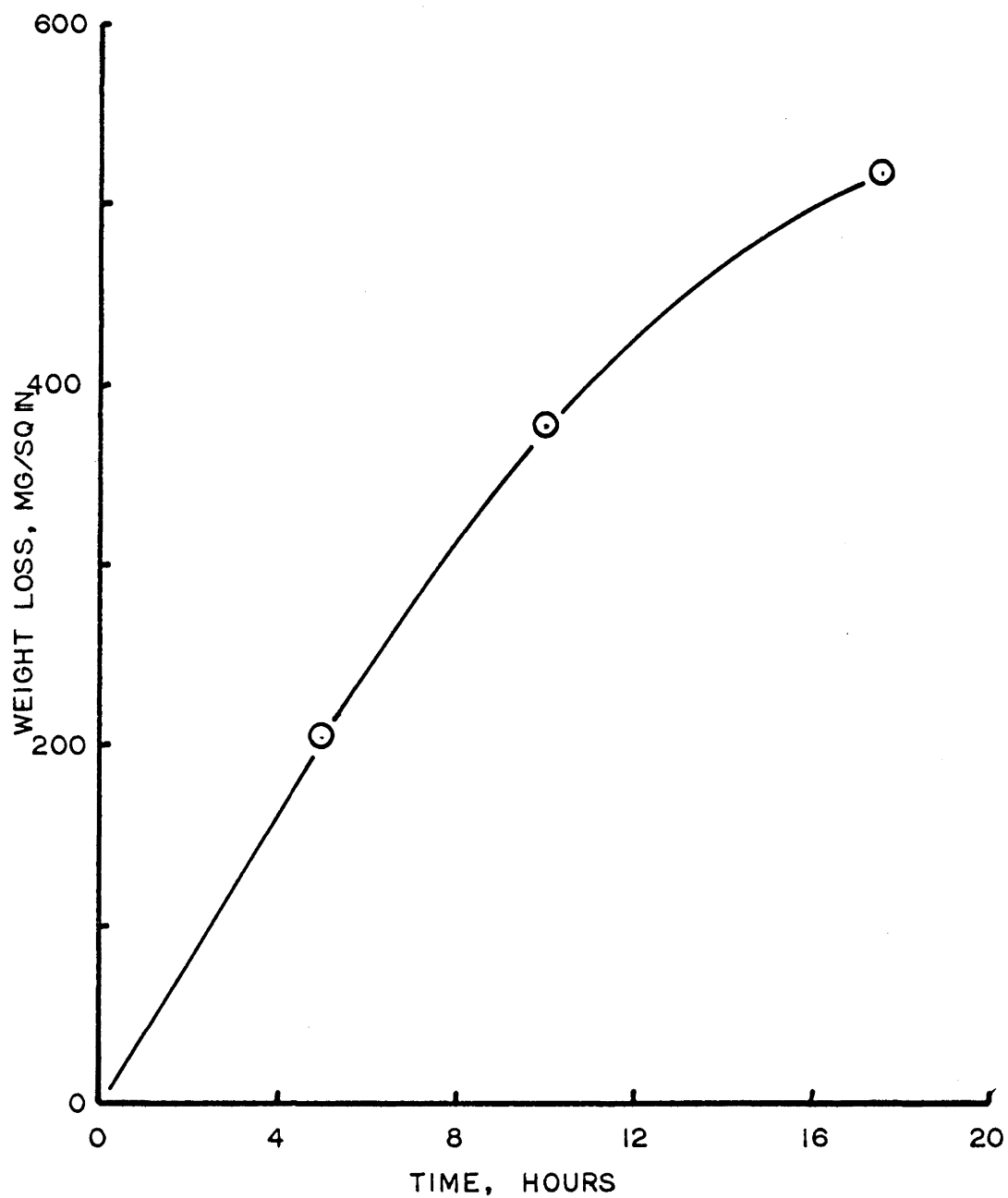


FIGURE 33. EFFECT OF PERIODIC SLAG ADDITION ON THE CORROSION OF 1020 CARBON STEEL BY AN 84 MOLE PER CENT VANADIUM PENTOXIDE-16 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

TABLE XVIII

THE CORROSION OF VARIOUS ALLOYS BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG IN A CARBON DIOXIDE ATMOSPHERE AT TEMPERATURES FROM 760 TO 927 DEGREES CENTIGRADE

TYPE METAL	TEMPERATURE	EXPOSURE TIME	SAMPLE AREA	CORRECTED WEIGHT LOSS
	°C	HRS	SQ IN	MG/SQ IN
HASTELLOY B	760	6.08	0.973	18.2
HASTELLOY B	760	11.67	1.098	28.3
HASTELLOY B	760	11.67	1.011	34.1
HASTELLOY B	760	17.92	0.944	41.4
HASTELLOY B	760	24.00	1.011	34.6
HASTELLOY B	760	30.25	0.958	38.5
HASTELLOY B	760	30.25	0.998	34.8
HASTELLOY B	760	35.84	0.922	39.6
HASTELLOY B	843	5.58	0.930	23.5
HASTELLOY B	843	11.58	0.944	29.7
HASTELLOY B	843	12.33	0.958	47.5
HASTELLOY B	843	18.00	0.972	38.0
HASTELLOY B	843	18.33	0.916	41.8
HASTELLOY B	843	24.00	1.005	52.5
HASTELLOY B	927	6.00	0.923	61.1
HASTELLOY B	927	11.84	0.950	70.1
HASTELLOY B	927	18.25	0.891	74.7
HASTELLOY B	927	24.08	0.936	102.8
HASTELLOY X	760	6.08	0.949	24.4
HASTELLOY X	760	11.67	0.935	36.9
HASTELLOY X	760	11.67	0.927	29.0
HASTELLOY X	760	17.92	0.935	42.9
HASTELLOY X	760	24.00	0.908	36.8
HASTELLOY X	760	30.25	1.025	60.9
HASTELLOY X	760	30.25	0.975	51.4
HASTELLOY X	843	6.08	0.927	26.0
HASTELLOY X	843	12.00	0.927	54.7
HASTELLOY X	843	12.00	0.922	50.6
HASTELLOY X	843	17.58	0.949	60.0
HASTELLOY X	843	24.50	0.975	55.5
HASTELLOY X	843	30.08	0.966	59.0
HASTELLOY X	843	30.08	0.912	57.1
HASTELLOY X	843	36.00	0.944	79.2
HASTELLOY X	927	5.16	0.966	14.7
HASTELLOY X	927	12.84	0.930	40.5
HASTELLOY X	927	12.84	0.988	37.8
HASTELLOY X	927	18.92	0.880	44.1
HASTELLOY X	927	24.00	0.882	51.9
HASTELLOY X	927	30.00	0.987	87.5
HASTELLOY X	927	30.00	0.908	73.1
HASTELLOY X	927	37.75	0.922	81.4
STAINLESS 347	927	6.25	0.960	15.6
STAINLESS 347	927	12.16	0.974	21.2
STAINLESS 347	927	12.16	1.034	18.7
STAINLESS 347	927	17.84	0.956	22.3
STAINLESS 347	927	24.42	1.011	43.3
STAINLESS 347	927	30.00	0.937	41.5
STAINLESS 347	927	30.00	1.024	49.1

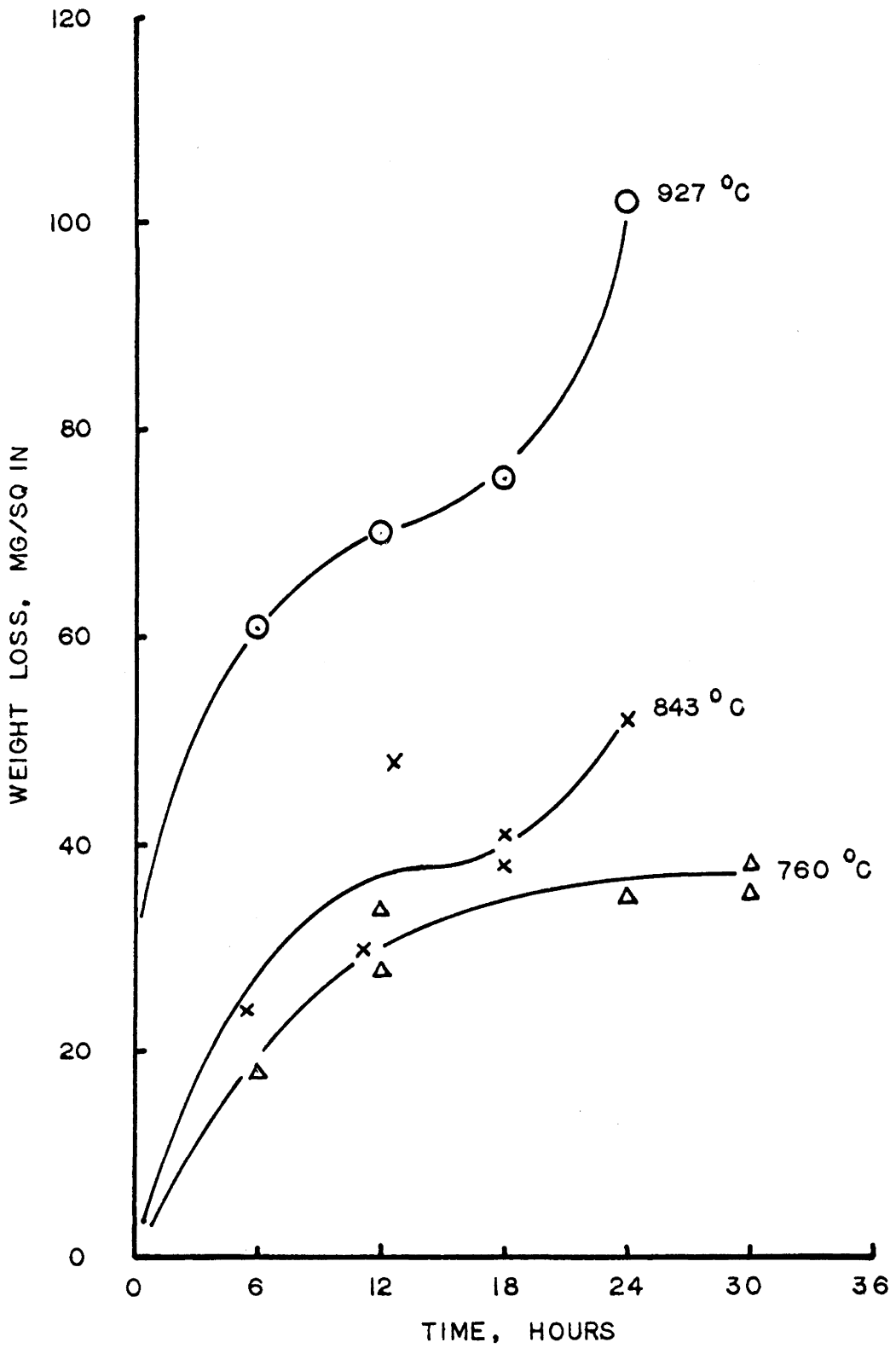


FIGURE 34. EFFECT OF TEMPERATURE ON THE CORROSION OF HASTELLOY B BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG IN CARBON DIOXIDE

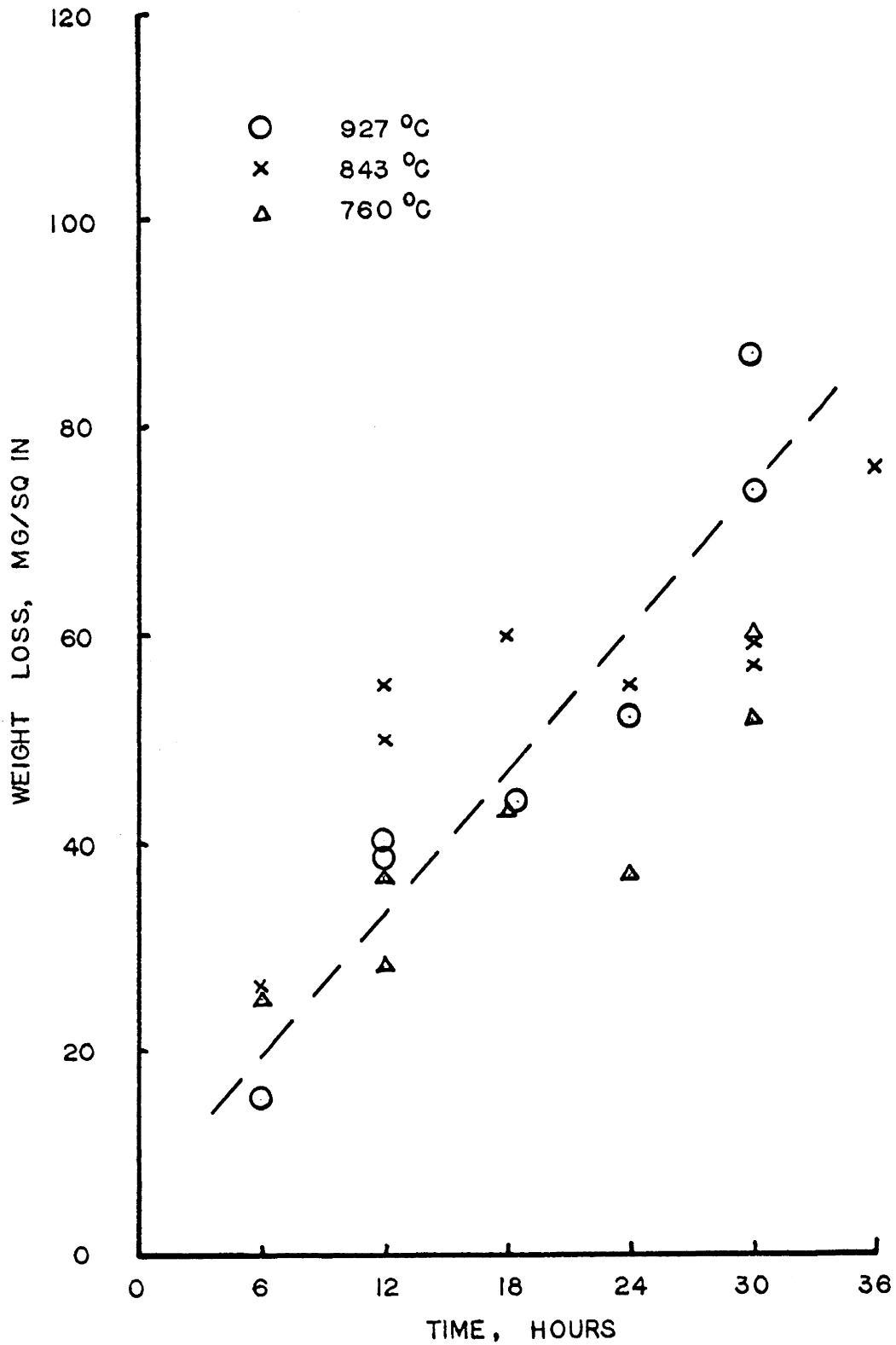


FIGURE 35. EFFECT OF TEMPERATURE ON THE CORROSION OF HASTELLOY X BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG IN CARBON DIOXIDE

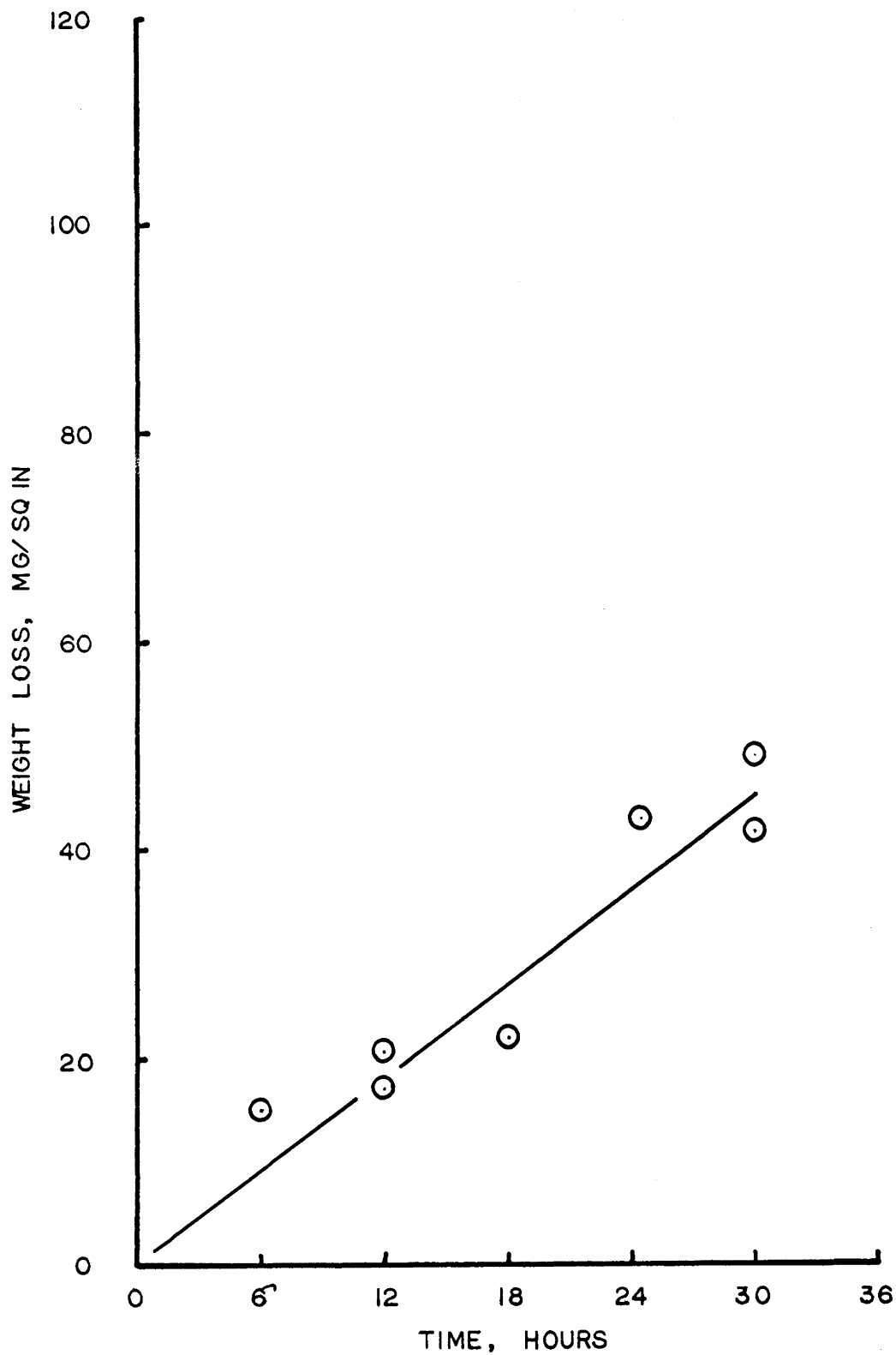


FIGURE 36. CORROSION OF 347 STAINLESS STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

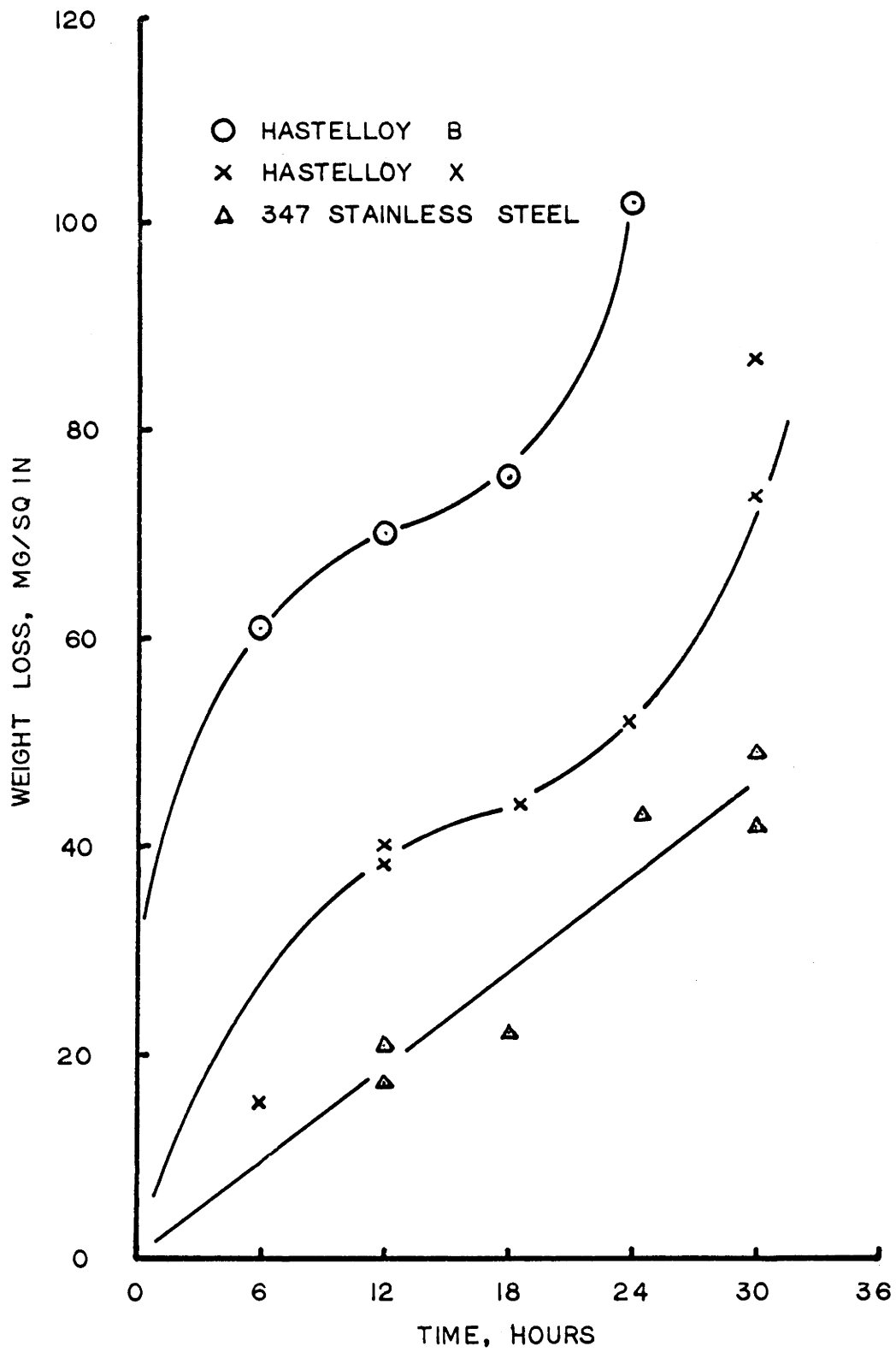


FIGURE 37. RELATIVE CORROSION OF HASTELLOY B, HASTELLOY X, AND 347 STAINLESS STEEL BY A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG AT 927 °C IN CARBON DIOXIDE

61 per cent, has the lowest corrosion resistance and as can be seen in Figure 34 the corrosion proceeds in a manner very similar to 1020 carbon steel in the presence of the same slag.

Analysis of Corrosion Products. X-ray diffraction patterns for the vanadium pentoxide and sodium carbonate used in these tests and for the products of corrosion from selected specimens are shown in Figures 38 through 40; with the exception of pure vanadium pentoxide and pure sodium carbonate, the x-ray diffraction patterns obtained had many lines which could not be explained by existing x-ray diffraction data. In general, however, the analysis of corrosion products indicates a reduction of the vanadium and simultaneous oxidation of iron.

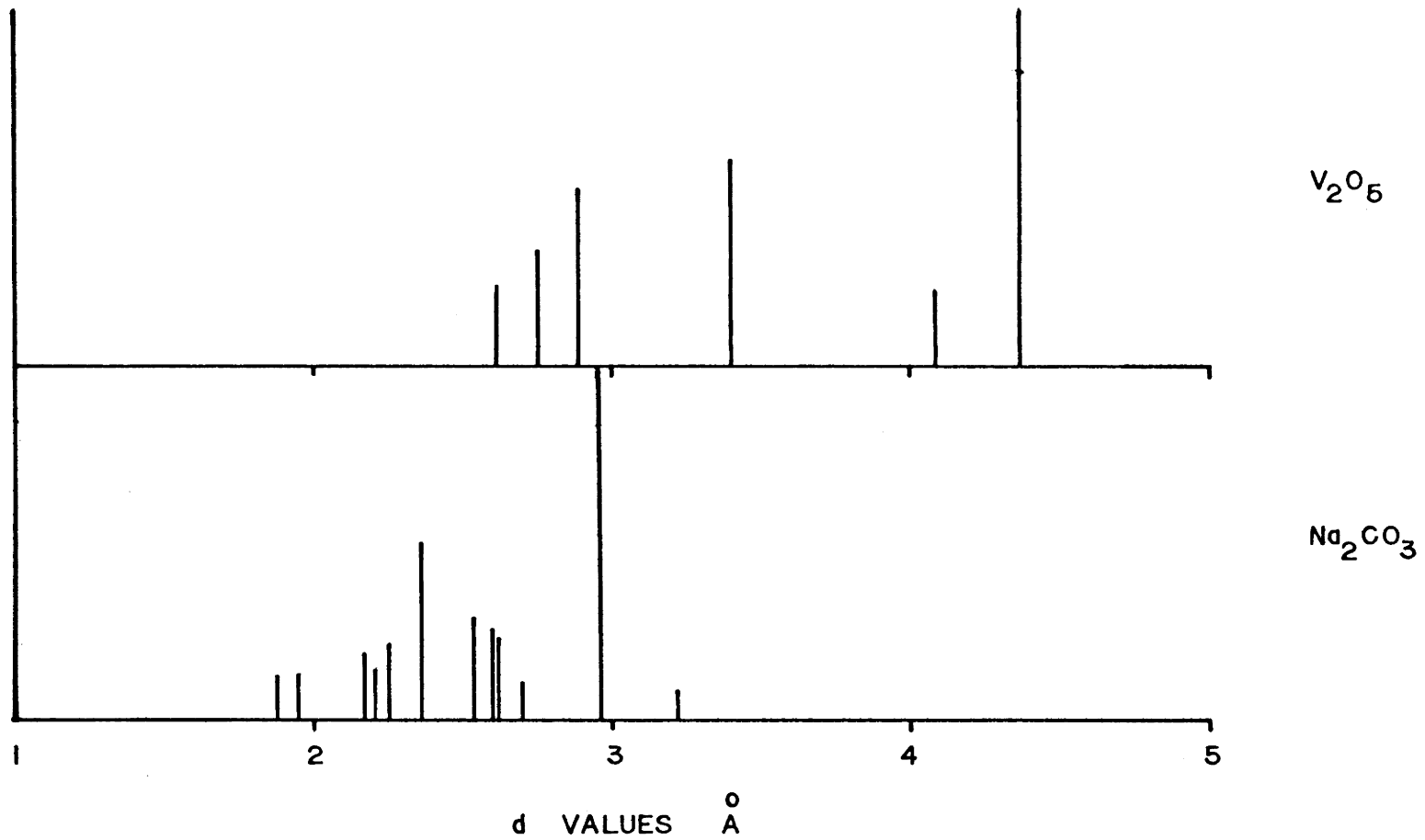


FIGURE 38. X-RAY DIFFRACTION PATTERNS FOR PURE COMPOUNDS

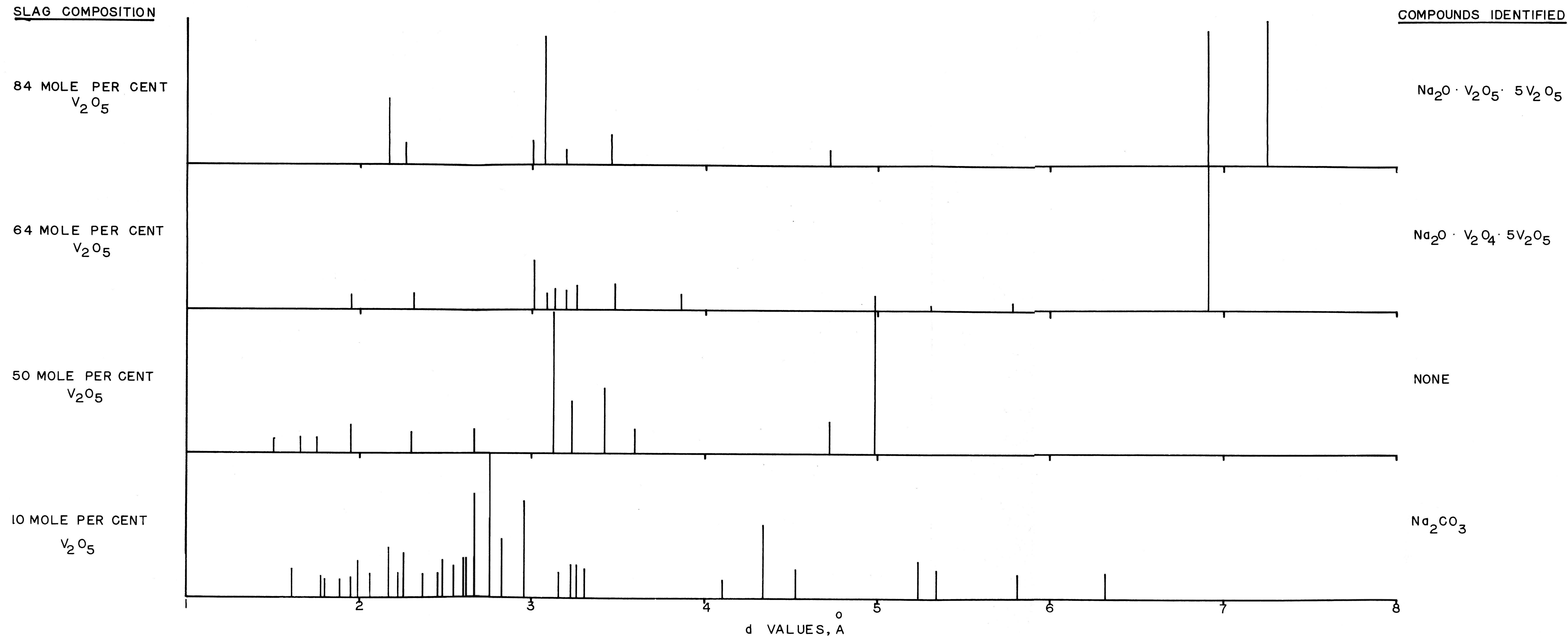


FIGURE 39. X-RAY DIFFRACTION PATTERNS FOR SLAGS

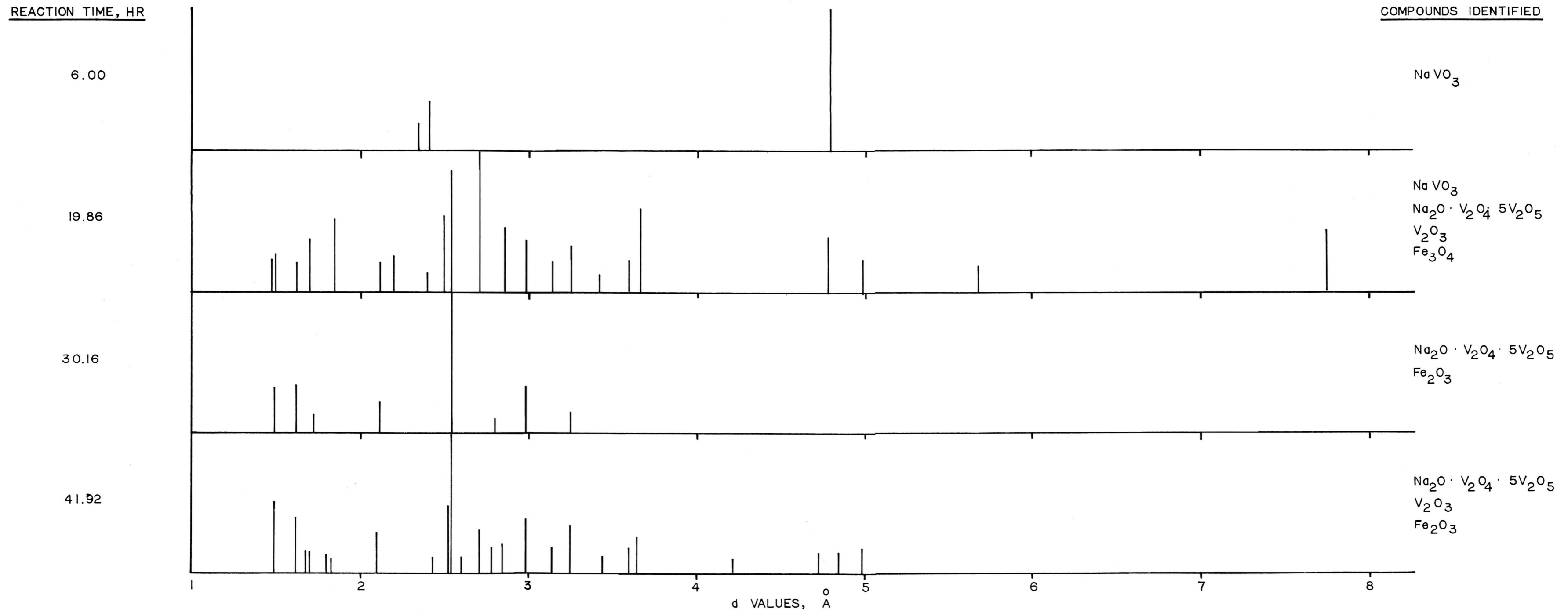


FIGURE 40. X-RAY DIFFRACTION PATTERNS OF CORROSION PRODUCTS FROM THE REACTION OF 1020 CARBON STEEL AND A 64 MOLE PER CENT VANADIUM PENTOXIDE-36 MOLE PER CENT SODIUM CARBONATE SLAG IN CARBON DIOXIDE

Sample Calculations

The following section includes samples of the calculations made for this investigation.

Area of Sample. The area of each sample was determined as follows:

$$A = 2(L \times W) + 2(L + W) T$$

where:

A = area of sample, sq in.

L = length of sample, in.

W = width of sample, in.

T = sample thickness, in.

Substituting data for sample 1, Table XI, page 69:

$$A = 2(0.875 \times 0.391) + 2(0.875 + 0.391) 0.05$$

$$A = 0.811 \text{ sq in.}$$

Corrected Weight Loss. To determine the weight loss by slag corrosion, it is necessary to determine the total weight loss and subtract the loss during cleaning as follows:

$$W_c = \frac{W_o - W_c}{A} - \frac{W_c - W_f}{A} \left(\frac{T_a}{T_b} \right)$$

where:

W_c = corrected weight loss, mg/sq in.

W_o = original sample weight, mg

W_c = cleaned sample weight, mg

W_f = final sample weight, mg

A = area of sample, sq in.

T_a = time in cleaning both to W_c , hr

T_b = time in cleaning between W_c and W_f , jr.

Substituting data for sample 1, Table XI, page 60:

$$W_c = \frac{2169.2 - 2145.1}{0.811} - \frac{2145.1 - 2144.1}{0.811} \left(\frac{6.0}{5.0} \right)$$

$W_c = 28.2$ mg/sq in.

Activation Energy. The energy of activation for constant slag composition was calculated by determining the slope of the straight line on the modified Arrhenius plots in Figures 11 and 22, pages 63 and 77, respectively. The equation of the straight line on an Arrhenius plot is:

$$\ln K = -\frac{E}{RT} + A$$

where:

- K = reaction rate constant, sec^{-1}
- E = activation energy, cal/mole
- R = universal gas constant, cal/deg-mole
- T = absolute temperature, °K
- A = constant.

The reaction rate is related to the reaction rate constant by the following relation:

$$r = Kc$$

where:

- r = reaction rate, mg/sq cm-min
- c = concentration, mole per cent.

Substituting this equation into the original Arrhenius equation and simplifying:

$$\ln r = - \frac{E}{RT} + \ln ca$$

The energy of activation is then expressed by the following relation:

$$E = - \left(\frac{\ln r}{(1/T)} \right) R$$

Substituting data from Figure 11, page 63:

$$E = - \left[\frac{(- 0.73) - (- 5.01)}{(0.00115) - (0.00083)} \right] 1.987$$

$$E = 26,600 \text{ cal/mole.}$$

IV. DISCUSSION

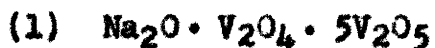
This section contains the discussion, recommendations, and limitations for this investigation.

Discussion of Literature

The following section is devoted to a discussion of the literature pertinent to the problem considered in this investigation.

Limitations of Previous Work. The majority of previous work was conducted in mixtures of sodium sulphate and vanadium pentoxide using steel alloys as specimens (1,14,17,24,30). Since sulphur is present in most crude oil, it is likely that sulphates exist in actual slag deposits. However, it was the object of this investigation to study the reaction of iron and molten mixtures of sodium and vanadium oxides, eliminating the sulphate variable. There is no reported work on the reaction of iron with molten mixtures of sodium and vanadium oxides.

Slag Composition. All previous work^(1,14,17,24,30) indicates that maximum corrosion occurs at a slag composition which favors the formation of:



For mixtures of sodium oxide or sodium carbonate and vanadium pentoxide this would be at vanadium pentoxide concentrations in excess of 50 mole per cent.

Slag Analysis. X-ray diffraction is the most frequently used technique for slag analysis; however, the almost complete lack of x-ray data on complex sodium-vanadium compounds makes analysis difficult. Only Foster, Liepold, and Shevlin⁽¹⁴⁾ have published data on the complexes formed at sodium to vanadium mole ratios of 1:3 and 1:6.

Corrosion Mechanism. Those previous investigators who postulated mechanisms generally considered the diffusion of components of the surrounding atmosphere through the slag to be the controlling mechanism. Several^(19,24) reported that they obtained no corrosion at all unless oxygen was present in the surrounding atmosphere.

Discussion of Procedure

The following section contains a discussion of the apparatus and procedure used in this investigation.

Furnace Construction. Originally an attempt was made to use ceramic furnace tubes and sample containers. However, the tendency for the molten slag to "creep" made it difficult to contain, and its low viscosity permitted it to penetrate the porous ceramic materials. On cooling, the difference in the thermal expansion characteristics of the tube material and the slag caused the tubes to crack.

All work was eventually done using 304 stainless steel combustion tubes and nickel sample holders. Since the slags tested attack both 304 stainless steel and nickel, some contamination resulted. The effect of this contamination was not determined. However, no evidence of nickel oxides or nickel vanadates was found in the x-ray diffraction patterns of the corrosion products removed from 1020 carbon steel specimens or the slags prepared in nickel crucibles; therefore, it was assumed that the effect of this contamination was negligible. To eliminate the possibility of

contamination, all work would have to be done in some more resistant metal, probably platinum.

Another major deficiency of the apparatus used was the necessity to open the furnace tube to move the sample holder into and out of the heated zone of the tube. Thus, although every precaution, as outlined in the procedure, was taken to prevent air from entering the system and to purge any air which may have entered, it was impossible to exclude all air. This is one explanation for the corrosion of samples heated without slag in a helium atmosphere.

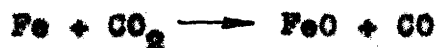
Temperature Control. As shown by Figure 8, page 55, the temperature difference between tubes averaged 12 °C over the temperature range of interest, with the temperature in the left hand tube always higher. The control temperature was maintained at the set point ± 5.5 °C. Variations greater than ± 5.5 °C and/or a noticeable change in the cyclic rate of temperature change usually indicated deterioration of the thermocouple.

Discussion of Results

The following section contains a discussion of the results obtained in this investigation.

Corrosion in the Absence of Slag. To establish a base, samples of 1020 carbon steel were heated in the furnace in both carbon dioxide and helium atmospheres. The results of these tests are shown in Table XI, page 60, and Figures 9 and 10, pages 61 and 62.

It has been previously reported ⁽¹³⁾ that the reaction between carbon dioxide and iron at temperatures above 649 °C proceeds:



The reaction apparently proceeds even at temperatures as low as 593 °C, since corrosion rates as high as 2.75 milligrams per square inch, hour, were observed at this temperature.

To obtain additional information on this reaction, an Arrhenius plot, Figure 11, page 63, was constructed and the activation energy for the reaction was determined to be 26,600 calories per mole of iron. Although the literature search did not produce a previously reported activation energy for this reaction,

the value obtained is of the order of magnitude reported for similar reactions.

The results of these tests shows clearly that carbon dioxide is an oxidizing atmosphere with respect to 1020 carbon steel at temperatures equal to or greater than 593 °C. At the highest and most frequently used temperature, 927 °C, the corrosion rate for 1020 carbon steel in a carbon dioxide atmosphere is 150 milligrams per square inch, hour.

Although helium should be an inert atmosphere with respect to 1020 carbon steel at the temperatures used in this study, corrosion did occur at a rate of 1.0 milligram per square inch, hour, at 593 °C, 2.3 milligrams per square inch, hour, at 760 °C, and 1.65 milligrams per square inch, hour, at 927 °C.

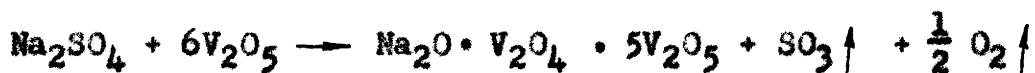
The fact that the rate is higher at 760 °C than at 927 °C illustrates the erratic character of the helium blank tests. Within a test, and particularly for a single set of four samples exposed in the same furnace tube, the data were consistent. Between tests, results were erratic. This indicates that air was being carried into the furnace when the tubes were opened to remove or replace samples.

Although the corrosion rate of 1020 carbon steel in helium was significant, the rate of carbon dioxide was as much as 90 times that in helium. Therefore, if the corrosion progresses by absorption of the gas by the slag, diffusion to the metal surface, and reaction of gas and metal, it should be evident by a difference in corrosion rate for tests conducted in the different gases.

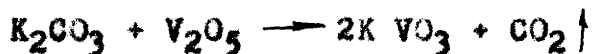
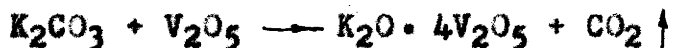
Corrosion by Slag at 593 °C. The results of tests made using 1020 carbon steel, a 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag, and both carbon dioxide and helium atmospheres at 593 °C are shown in Tables XII and XIII, pages 65 and 66, and Figures 12 and 17, pages 67 and 72.

The results obtained in these tests are unusual in that in both carbon dioxide and helium the variation of corrosion rate both within and between tests was much greater than at higher temperatures, and the rate at six hours or less is equal to or greater than the rates at similar conditions, but at higher temperatures.

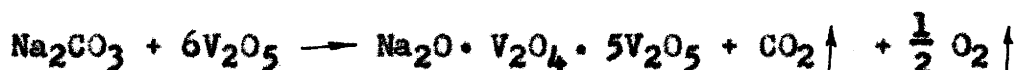
Since previous investigators^(10,19) have shown that:



and that:



it is reasonable to assume that reactions of the type:



also occur. This assumption is substantiated by x-ray diffraction analysis of a slag composed of 64 mole per cent vanadium pentoxide and 36 mole per cent sodium carbonate. The results of the analysis is shown in Figure 39, page 103. The only identifiable compounds present are the sodium vanadyl vanadates:

$\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ and $5\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$. The absence of sodium vanadate in the slag mixture and the strong evidence of $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, indicates that the actual composition of the slag is not that determined from the weight of the components, but is higher in vanadium pentoxide content. This could occur, if, during the original slag preparation some sodium carbonate decomposed with the loss of both

sodium oxide and carbon dioxide. Since sodium carbonate decomposes at temperatures as low as 400 °C and sodium oxide sublimes, loss of sodium carbonate in this manner is possible.

A shift to higher vanadium pentoxide content would raise the melting point of the slag. Therefore, one explanation for the erratic results of the tests conducted at 593 °C is that cyclic fluctuations in furnace temperature resulted in the alternate melting and solidification of all or portions of the slag system on some samples. When the slag was solid, the corrosion rate would be low; however, the cycling from liquid to solid could cause the corrosion products to break away from the surface of the specimen, thus exposing clean metal surface to corrosion. This latter fact may explain the unusually high corrosion rates observed in some of the tests conducted at 593 °C.

Since the results indicate that the slag in tests conducted at 593 °C did not remain molten but continuously cycled from completely molten to at least partially solid, the results of these tests are not considered directly comparable to results of tests

conducted at higher temperatures where the slag remained molten during the entire tests.

Effect of Temperature. A series of tests were conducted using 1020 carbon steel, a slag composed of 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate, atmospheres of both carbon dioxide and helium, and temperatures of 677, 760, 843, and 927 °C. The results of these tests are given in Tables XII and XIII, pages 65 and 66, and represented by the curves shown in Figures 12 to 21, pages 67 to 76.

In all tests, regardless of temperature, the average rate of corrosion for the first six hours was approximately 19 milligrams per square inch, hour. At 677 °C in carbon dioxide atmosphere, the rate from 6 to 36 hours dropped to 1.3 milligrams per square inch, hour. At 677 °C in helium, the rate also dropped sharply after six hours; however, at 24 hours, the rate began to increase with the average rate from 24 to 36 hours being 5.7 milligrams per square inch, hour. At 760 °C in both carbon dioxide and helium the initial rapid rate for the first six hours is followed by a 12 hour period in which little or no corrosion takes place. At 18 hours the rate increases to 5.6 milligrams per square inch, hour. At 843 °C and 927 °C in both

carbon dioxide and helium, the plot of weight loss versus time is a smooth curve classic of a corrosion reaction in which one reactant is being depleted.

The break in the curves at intermediate temperatures, Figures 14, 18, and 19, pages 69, 73, and 74, could be the result of two phenomena. First, if the rapid initial reaction leaves a layer of corrosion products on the metal surface, these deposits must be fluxed away or the molten slag must diffuse through it before further corrosion by the slag can proceed. Second, if the total corrosion is a combination of initial corrosion by the slag and subsequent corrosion by the gas diffusing through the slag, a curve such as those obtained is also possible. Since corrosion in both carbon dioxide and helium was very similar and since the weight loss appears to reach a maximum at about 200 to 220 milligrams per square inch, the first explanation is the more realistic.

Arrhenius plots for each set of data are shown in Figure 21, page 76. The reaction rates were determined from the slope of the weight loss versus time curve at 140 milligrams per square inch weight loss. From these plots, the activation energy in carbon dioxide was

found to be 18,300 calories per mole and in helium, 17,400 calories per mole. Since there is no significant difference in these two values, the two reactions may be similar.

Effect of Pressure. In addition to the test at atmospheric pressure in carbon dioxide atmosphere, Figure 15, page 70, tests were also made at 15 and 28 pounds per square inch, gage, using 1020 carbon steel, 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag and a temperature of 927 °C. The results are given in Table XVI, page 91, and Figure 32, page 92. Increasing the carbon dioxide pressure had no significant effect on corrosion. This is additional proof that the atmosphere surrounding the sample has little or no effect on corrosion. This is quite different from the work reported by Johnson⁽²⁹⁾ in which corrosion of stainless steels by molten sodium sulphate-vanadium pentoxide slags occurred only when oxygen was present in the atmosphere. He observed no corrosion in nitrogen and helium atmospheres.

Effect of Slag Composition. A series of tests was made using 1020 carbon steel, both carbon dioxide and helium atmospheres, a constant temperature of

927 °C, and slags containing 16, 36, 50, 90, and 100 per cent sodium carbonate. The results of these tests are given in Tables XIV and XV, pages 79 and 80, and Figures 23 to 30, pages 81 to 88.

Slags of 100 mole per cent sodium carbonate decomposed and vaporized completely from the specimen surface in 30 hours in both carbon dioxide and helium. As discussed earlier, the sodium carbonate decomposes to sodium oxide and the sodium oxide sublimates. Slag containing 10 mole per cent vanadium pentoxide also evaporated from the specimen; however, some residual slag remained for the duration of the tests.

A plot of initial reaction rate versus slag composition is shown in Figure 31, page 89. For slag compositions equal to or greater than 50 mole per cent vanadium pentoxide, the difference in corrosion rate between tests conducted in carbon dioxide and helium is small with this corrosion rate increasing from 17 to 20 milligrams per square inch, hour, to 66 milligrams per square inch, hour, as the vanadium pentoxide content increases from 50 to 84 mole per cent. The primary reaction at these conditions is the oxidation of iron with reduction of vanadium.

For 100 mole per cent sodium carbonate slag, the evaporation of the slag exposed the metal surface to the carbon dioxide, thus the high corrosion rate of 55 milligrams per square inch, hour. This corrosion rate was constant for the duration of the test, 36 hours. The fact that this rate is less than the rate of 160 milligrams per square inch, hour, for an unslagged sample, at similar conditions, shows that the slag retarded the attack by carbon dioxide.

For 90 mole per cent sodium carbonate-10 mole per cent vanadium pentoxide slag, the corrosion in carbon dioxide increased to 123.5 milligrams per square inch, hour. The increase in rate over that observed for 100 mole per cent slag can be explained by the fluxing of the corrosion products by the residual slag; thus, making it easier for the carbon dioxide to reach the metal surface.

Corrosion in helium at slag compositions of 0 to 50 mole per cent vanadium pentoxide ranged from 7 to 17 milligrams per square inch, hour. The corrosion rate, which is significantly higher than the 1.7 milligrams per square inch, hour, observed with no slag, may result from attack by carbon dioxide formed by

decomposition of sodium carbonate or by oxidation by vanadium oxides.

It is interesting to note that the relationship between initial reaction rate versus slag composition for iron in sodium carbonate-vanadium pentoxide slags and carbon dioxide, shown in Figure 31, page 89, does not resemble a curve⁽¹⁶⁾ for the corrosion of alloy JA-5 (chromium-nickel steel) in mixtures of sodium sulphate and vanadium pentoxide, and air, Figure 5, page 32. This is not surprising since the protective oxide film on the surface of the stainless steel would protect the specimen until sufficient vanadium pentoxide is present to act as a flux. Also, the phase diagram for the system sodium sulphate-vanadium pentoxide, Figure 4, page 23, is quite different from that for sodium oxide-vanadium pentoxide. In neither case does maximum corrosion occur at an eutectic.

The corrosion problem studied in this investigation became apparent in industrial applications when the metal surfaces in contact with the slag reached a temperature of 550 to 600 °C and the sodium-vanadium ratio in the slag approached the eutectic composition with a melting point of 525 °C. One technique for

combatting this corrosion has been to alter the slag composition, possibly by water washing the crude to remove sodium, to increase the melting point.

Since the trend is to higher and higher metal temperatures, and the results of this and other investigations show that corrosion rates may increase as the slag composition is varied from the eutectic composition, it may prove impractical to combat the problem by altering slag composition.

Effect of Atmosphere at Constant Slag Composition.

The series of tests made to determine the effect of temperature on the corrosion of 1020 carbon steel by a 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag, Tables XII and XIII, pages 65 and 66, was conducted in both the oxidizing atmosphere, carbon dioxide, and the inert atmosphere, helium. At temperatures of 843 °C or less, there is no significant difference between the tests conducted in the different gases. At 927 °C the initial rates of corrosion are also equal in both gases; however, at times from 6 to 30 hours the rate in carbon dioxide is nearly constant at 5.4 milligrams per square inch, hour, while the rate in

helium decreases steadily and averages only 3.5 milligrams per square inch, hour.

In the discussion on the effect of atmosphere at a constant temperature at 927 °C and various slag compositions, it was pointed out that as the vanadium pentoxide content of the slag decreased the rate of corrosion in carbon dioxide increased. X-ray diffraction data indicate a reduction of vanadium with the formation of free vanadium trioxide and tetroxide during the corrosion process. This formation of free vanadium oxides may result in an effective slag composition with significantly lower vanadium pentoxide content and thus account for the higher rate of corrosion in carbon dioxide.

Periodic Slag Addition. Further proof that a component of the slag and not the atmosphere is the major cause of corrosion, was obtained by redipping the specimens in fresh slag every five hours. When fresh slag is added, the weight loss versus time curve does not level off at 200 to 220 milligrams per square inch, but corrosion continues at a nearly constant rate of 29.5 milligrams per square inch, hour, as shown in Table XVIII, page 96, and Figure 33, page 95.

If Figure 26, page 84, and Figure 33, page 95, are compared, it is obvious that the curve in Figure 33 should progress step-wise from point to point rather than as a smooth curve.

X-Ray Analysis. The x-ray diffraction patterns for the pure compounds vanadium pentoxide and sodium carbonate, slags composed of various ratios of these two compounds, and corrosion products formed when these slags corrode 1020 carbon steel are shown in Figures 38 through 40, pages 102 through 104.

Analysis of the patterns for the slags, Figure 39, indicates free sodium carbonate exists in the slag containing 10 mole per cent vanadium pentoxide. Slags containing 64 and 84 mole per cent vanadium pentoxide contained the complex sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$. No identifiable compounds were found in the 50 mole per cent vanadium pentoxide slag. All diffraction patterns had unidentifiable lines.

The diffraction patterns for the corrosion products, Figure 40, show the general trend of vanadium being reduced and iron being oxidized.

It is obvious that products other than sodium vanadate must be present in the corrosion products

after six hours; however, duplicate diffraction patterns failed to produce evidence of any other compounds. It is possible that the very strong response to the sodium vanadate masked the presence of other compounds which may have been present or the sensitivity of the x-ray techniques and equipment used may have been too low.

Vanadium trioxide was definitely identified at 19.86 and 41.92 hours; however, at 30.16 hours although there was some evidence of vanadium trioxide, it was not sufficient to prove definitely its presence.

From 19.86 hours on, there is very strong evidence that the iron in the slag is being oxidized from ferrosferric to ferric oxide.

The lack of complete x-ray data on the metal complexes formed in the slags has greatly reduced the value of these patterns in determining the exact corrosion mechanism. Further work on this corrosion problem should be preceded by an extensive study on identifying the products of corrosion.

Mechanism. Since it has been established that the primary corrosion reaction is between components of the molten slag and the metal surface, a material balance and the analysis of corrosion products shown in

Figure 40, page 104, were used to develop the following mechanism.

Each specimen was coated with approximately 1.35 grams of slag per square inch. The only compound detected in the corrosion products after six hours was sodium vanadate. During the first six hours approximately 100 milligrams per square inch of sample was reacted. Therefore, if it is assumed that iron is converted to ferrous oxide and sodium is converted to sodium vanadate, the mole ratio of the residual vanadium and oxygen is 1:2, indicating that vanadium pentoxide has been reduced to vanadium tetroxide.

As the reaction progresses new iron is oxidized and the ferrous oxide in the slag is further oxidized to ferrosferric oxide and then to ferric oxide while the vanadium is reduced from a valence of + 5 to + 3, and + 4. This mechanism is substantiated by analysis of corrosion products at 19.86, 30.16, and 41.92 hours. At 19.86 hours the concentration of sodium vanadate has been greatly reduced and vanadium trioxide, the sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, and ferrosferric oxide appear. At 30.16 hours only ferric oxide and $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ are identifiable, and at 41.92 hours

the corrosion products contain vanadium trioxide, ferric oxide, and $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$.

At 41.92 hours the weight of iron reacted is approximately 200 milligrams per square inch. Assuming all iron oxidized to ferric oxide and all sodium as sodium oxide, the average valence of the vanadium must be + 3.32 thus accounting for the strong vanadium trioxide peaks.

Effect of Alloy Composition. In addition to the work done with 1020 carbon steel, tests were conducted using Hastelloy B, Hastelloy X, and 347 stainless steel in a 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag and a carbon dioxide atmosphere.

Figure 37, page 100, shows the relative corrosion of the three alloys at 927 °C. Hastelloy X, Hastelloy B, and 347 stainless steel corrode at an average rate of 4.3, 2.2, and 1.7 milligrams per square inch, hour, respectively. These rates are proportional to the nickel content and to the nickel-chromium ratio, indicating strongly that alloys for service where slag corrosion is a problem should be low in nickel content.

The nature of the corrosion of Hastelloy X, which contains 61 per cent nickel, is very similar to the attack on 1020 carbon steel by the 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag. The initial attack is very rapid, followed by a period of lower rate, and finally by a period of higher rate. For Hastelloy X at 927 °C, the initial rate, intermediate rate, and final rate are 10.0, 1.25, and 4.7 milligrams per square inch, hour, respectively. The mechanism for this attack is probably similar to that discussed earlier for the corrosion of 1020 carbon steel.

At 760 °C, the Hastelloy X corrodes at a rate of 2.7 milligrams per square inch, hour, for the first 11 hours, after which the rate becomes negligible. This is similar to the corrosion of 1020 carbon steel at 593 °C.

Recommendations

The following recommendations are made as a result of the tests conducted during this investigation of the corrosion of steels by molten mixtures of vanadium pentoxide and sodium carbonate.

X-Ray Diffraction Data. Studies must be made to determine x-ray diffraction data on the complex compounds of sodium, vanadium, iron, nickel, and chromium found in the products of corrosion. With the information now available, x-ray diffraction analysis of the products of corrosion is limited. Complete x-ray data on all possible complex compounds would make both x-ray diffraction and electron microprobe analysis of corrosion products very useful tools in the study of these corrosion reactions.

Slag Characteristics. At present, little is known of the physical properties, diffusion characteristics, and electrical properties of the slags studied. Investigations should be conducted to supply this information. The effect of products of corrosion on the phase diagram of the slags would be of particular interest. High temperature differential thermal

analysis equipment now available could be used very effectively in this area.

Slag Composition. The results of this investigation indicate that the corrosion rate of 1020 carbon steel in a carbon dioxide atmosphere reaches a maximum when the slag contains less than 50 mole per cent vanadium pentoxide. It is recommended that a more detailed study be made of the corrosion reaction at these conditions.

Presence of Sulphate. The presence of sulphates may affect the corrosion of 1020 carbon steels by molten sodium-vanadium slags. It is recommended that this effect be investigated.

Continuous Slag Addition. This investigation demonstrated that the direct reaction between the slag and steel is the most significant in the corrosion process. Tests should be conducted such that fresh slag is continuously supplied and the products of corrosion are continuously removed. Tests of this type will provide data more adaptable to thermodynamics and kinetic consideration.

Gas Diffusion. To study further the effect of gas diffusion through the slag, tests should be made

at pressures in excess of the maximum of 28 pounds per square inch, gage, used in this investigation.

Equipment. The combustion tubes, sample holders, and slag preparation containers should be constructed of material which is not attacked by the slags used. Platinum is the only material meeting this requirement.

The furnace should be redesigned to completely eliminate air entering the system when samples are added or removed.

The furnace should be redesigned to permit higher gas pressures in the furnace tube.

Limitations

The investigation was performed under the following limiting conditions.

Sample Size. All samples used in the corrosion tests were approximately 0.750 inch long by 0.500 inch wide. All samples were 0.050 inch thick.

Sample Composition. Tests were conducted using 1020 carbon steel, Hastelloy B, Hastelloy X, and 347 stainless steel.

Slag Composition. Slags composed of 100 per cent sodium carbonate, 10 mole per cent vanadium

pentoxide-90 mole per cent sodium carbonate, 50 mole per cent vanadium pentoxide-50 mole per cent sodium carbonate, 64 mole per cent vanadium pentoxide-36 per cent sodium carbonate, and 84 mole per cent vanadium pentoxide-16 mole per cent sodium carbonate were used in this investigation.

Temperature. Tests were conducted at 593, 677, 760, 843, and 927 °C using a 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate slag.

Pressure. Tests were conducted in a carbon dioxide atmosphere at 0.0, 15.0, and 28.0 pounds per square inch, gage.

Time. Samples were corroded for a maximum of 36 hours. Intermediate samples were taken at six-hour intervals.

Atmosphere. Tests were conducted in both carbon dioxide and helium atmospheres.

Corrosion Product Analysis. The products of corrosion removed from the metal sample were analyzed by standard x-ray diffraction techniques.

V. CONCLUSIONS

The investigation of the corrosion of 1020 carbon steel, Hastelloy B, Hastelloy X, and 347 stainless steel by molten mixtures of vanadium pentoxide and sodium carbonate was conducted in a standard two-tube combustion furnace. Samples of steel 0.750 by 0.500 inch, 0.050 inch thick were coated with molten slag and maintained at a constant temperature of 593, 677, 760, 843, or 927 °C for 6, 12, 18, 24, 30, and 36 hours. Slag compositions of 100, 90, 50, 36, and 16 mole per cent sodium carbonate were used. The tests were conducted in both carbon dioxide and helium. Tests in carbon dioxide were conducted at 0.0, 15.0, and 28.0 pounds per square inch, gage. The experimental results led to the following conclusions:

1. The nickel sample holders and 304 stainless steel combustion tubes were severely attacked by the slags used in this investigation.
2. Carbon dioxide is corrosive to 1020 carbon steel at temperatures equal to or greater than 593 °C.
3. The rate of corrosion of 1020 carbon steel by carbon dioxide increases with increasing temperature.

4. The activation energy for the reaction of carbon dioxide and 1020 carbon steel is 26,600 calories per mole of iron.

5. The rate of corrosion of 1020 carbon steel coated with a 64 mole per cent vanadium pentoxide slag and heated in both carbon dioxide and helium atmospheres increased with increasing temperature.

6. The corrosion of 1020 carbon steel by a 64 mole per cent vanadium pentoxide slag was not significantly different in helium and carbon dioxide at temperatures equal to or less than 843 °C.

7. The corrosion of 1020 carbon steel by a 64 mole per cent vanadium pentoxide slag in carbon dioxide at 927 °C was greater than that in helium.

8. In carbon dioxide at 927 °C, maximum corrosion rates for 1020 carbon steel occur at a slag composition of 10 mole per cent vanadium pentoxide.

9. In helium at 927 °C maximum corrosion rates for 1020 carbon steel occur at slag compositions of 84 mole per cent vanadium pentoxide.

10. The effect of carbon dioxide on the corrosion of 1020 carbon steel at 927 °C decreases as the vanadium pentoxide content of the slag increases.

11. The corrosion of steel by a 64 mole per cent vanadium pentoxide slag results from the oxidizing properties of the vanadium oxides, with the reaction proceeding: (1) initial oxidation of steel to ferrous oxide with reduction of vanadium pentoxide to vanadium tetroxide, (2) fluxing of the initial products of corrosion by the slag, and (3) simultaneous additional oxidation of the metal specimen and oxidation of the ferrous oxide dissolved in the slag to ferrosiferrous and ferric oxide with further reduction of vanadium to vanadium trioxide.

12. As the nickel content of the chromium-nickel-iron alloys tested increased from 12.5 per cent (347 stainless steel) to 61.0 per cent (Hastelloy B), the initial corrosion rate by a 64 mole per cent vanadium pentoxide slag in carbon dioxide at 927 °C increased from 1.7 milligrams per square inch, hour, to 10.0 milligrams per square inch, hour.

VI. SUMMARY

The problem of corrosion of steels by slags deposited during combustion of heavy petroleum fuels which contain sodium and vanadium becomes very severe when the temperature of the metal exceeds 550 to 600 °C, thus placing undesirable limitations on both the manufacturers and users of heavy fuel oil fired boilers and turbines. To contribute to the understanding of this problem, this study was made to determine the mechanism of the reaction between iron and molten mixtures of sodium and vanadium oxides.

Tests were conducted on 1020 carbon steel in carbon dioxide and helium atmospheres at temperatures from 593 °C to 927 °C using a slag composed of 64 mole per cent vanadium pentoxide-36 mole per cent sodium carbonate, and at 927 °C using sodium-vanadium slags with 100, 90, 50, 36, and 16 mole per cent sodium carbonate. Tests were also made with Hastelloy B, Hastelloy X, and 347 stainless steel. The metal specimens were coated with the slag, heated at a constant temperature in a combustion furnace for up to 36 hours, and cleaned and weighed to determine

weight loss. The slag and corrosion products were analyzed by x-ray diffraction techniques.

The 64 mole per cent vanadium pentoxide slag was chosen for the most extensive study since it represents the primary eutectic of the sodium oxide-vanadium pentoxide system and favors the formation of the complex sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, considered by many investigators to be the major cause of corrosion.

This work showed that the corrosion reaction results from the oxidation of iron by vanadium oxides, with the reaction proceeding as follows: (1) oxidation of iron to ferrous oxide with reduction of vanadium pentoxide to the tetroxide, (2) fluxing of the initial products of corrosion by the slag, and (3) simultaneous additional oxidation of iron and further oxidation of ferrous oxide to ferrosferric and ferric oxide. At intermediate temperatures, 670 °C, step (2) controls the corrosion rate for a portion of the reaction, as evidenced by two very distinct changes in slope of the weight loss-time curve. At higher temperatures, 927 °C, no distinct changes in slope were observed.

Tests at various slag compositions show that the effect of carbon dioxide increases as the sodium carbonate concentration of the slag increases. Above a one to one mole ratio, increasing the vanadium pentoxide content of the slag increases the rate of corrosion. At 50 mole per cent vanadium pentoxide the rate of corrosion of 1020 carbon steel was approximately 17 milligrams per square inch, hour, while at 84 mole per cent vanadium pentoxide the rate was 65 milligrams per square inch, hour.

The tests conducted with alloy steels show that increasing the nickel content of the alloy from 12.5 to 61.0 per cent, increases the corrosion rate from 1.7 to 10.0 milligrams per square inch, hour.

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VIII. ACKNOWLEDGMENTS

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The author would particularly like to thank his wife and son for their understanding and encouragement during these most difficult years, and his parents for their continuous faith and support.

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APPENDIX

Materials

The materials utilized in this investigation are listed in the following paragraphs.

Acetone. Technical grade. Manufactured by Fisher Scientific Company, Pittsburgh, Pa. Used to dry metal specimens after cleaning.

Carbon Dioxide. Compressed, extra dry, industrial grade, pressure 2500 psig. Obtained from Southern Oxygen Company, Roanoke, Va. Used in carbon dioxide atmospheric tests.

Emery Cloth. Grade, fine. Obtained from Blacksburg Hardware Store, Blacksburg, Va. Used for rough polishing metal specimen.

Hastelloy B. Commercial grade, 0.05 in. thick, sheet. Obtained from the Haynes Stellite Company, Division of Union Carbide Corporation, Kokomo, Ind. Used as sample material in the corrosion tests.

Hastelloy X. Commercial grade, 0.05 in. thick, sheet. Obtained from Haynes Stellite Company, Division of Union Carbide Corporation, Kokomo, Ind. Used as sample material in corrosion tests.

Helium. Compressed, pressure 2500 psig. Obtained from Southern Oxygen Company, Roanoke, Va. Used in helium atmosphere tests.

Hydrochloric Acid. Technical grade. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J. Used to clean metal specimens.

Hydrofluoric Acid. Technical grade, 52 per cent. Obtained from Fisher Scientific Company, Fair Lawn, N. J. Used to clean metal specimens.

Nitric Acid. Technical grade. Obtained from Fisher Scientific Company, Fair Lawn, N. J. Used to clean metal specimens.

Polishing Paper. Grade, 400 A. Obtained from Blacksburg Hardware Store, Blacksburg, Va. Used to polish metal specimens.

Rodine 120. Pickling acid inhibitor. Manufactured by Anchem Products, Inc., Ambler, Pa. Used to inhibit the hydrochloric acid cleaning bath.

Sodium Carbonate. Anhydrous-granular, Baker "Analysed" reagent. Manufactured by J. T. Baker Chemical Company, Phillipsburg, N. J. Used in the preparation of slags.

Carbon Steel, 1020. Commercial grade, 0.05 in. thick, cold rolled. Ladle analysis given in Table VII. Obtained from American Steel and Wire Division, United States Steel Corporation, Cleveland, Ohio. Used as sample for corrosion tests.

Stainless Steel, 347. Commercial grade, 0.05 in. thick. Obtained from the sheet metal shop, Hercules Powder Company, Radford Ordnance Works, Radford, Va. Used as samples for corrosion tests.

Tubing, 304 Stainless Steel. Outside diameter 1-1/4 inches. Obtained from Whitehead Metal Products Company, Inc., Baltimore, Md. Used to make tubes for the combustion furnace.

Vanadium Pentoxide. Anhydrous Fisher "Certified" reagent. Obtained from Fisher Scientific Company, Silver Spring, Md. Used in preparation of slags.

Apparatus

The following apparatus was utilized in this investigation.

Ammeter. One, Weston, range 0-15 amp, graduated in 0.5 amp increments. Obtained from Fisher Scientific Company, Fair Lawn, N. J. Used to measure the current flow to the Hoskins electric furnace.

Analytical Balance. Chain-o-matic, model 220-D, serial No M-16011, capacity 200 gm, sensitivity ± 0.0001 gm. Manufactured by Volland and Sons, Inc., New Rochelle, N. Y. Used to weigh metal specimens.

Combustion Barges. Thirty-six, nickel combustion barges, catalog 7-647. Obtained from Fisher Scientific Company, Silver Spring, Md. Used as carriers for the metal specimens while they were in the combustion furnace.

Crucibles. Twelve, 50 ml, nickel, catalog 8-020. Obtained from Fisher Scientific Company, Silver Spring, Md. Used as containers for preparation of the slags.

Furnace, Hoskins. One, type FE 104, serial No 39159, 110 v, 1.9 amp, electric. Manufactured by Hoskins Manufacturing Company, Detroit, Mich. Used to melt the slags for application to the metal specimens.

Furnace, Veritemp, Combustion. One, 115 v, one ph, 50-60 cy, 13 amp, serial No 34838. Manufactured by Harry W. Dietert Company, Detroit, Mich. Used to heat the metal specimens during corrosion tests.

Gage. One, test quality, 0-30 psig, graduated in 0.1 psi increments. Manufactured by Manning, Maxwell and Moore, Instrument Division, Stratford, Conn. Used to measure the gas pressure in the furnace tubes.

Galvanometer. One, catalog 570-201. Manufactured by G-M Laboratories, Inc., Chicago, Ill. Obtained from Fisher Scientific Company, Fair Lawn, N. J. Used to measure current flow in the potentiometer-thermocouple circuit.

Glassware. Miscellaneous beakers and flasks. Obtained from Fisher Scientific Company, Silver Spring, Md. Used as containers for cleaning metal specimens and various other work.

Potentiometer. One, type S, with ranges of 0-1.7 volts in millivolt increments and 0-17 millivolts in 0.01 millivolt divisions. Obtained from Fisher Scientific Company, Pittsburgh, Pa. Used to measure emf generated by thermocouples.

Recorder-Controller. One, Tagliabue celestray, range 0-1800 °F in 10° increments, for iron-constantan thermocouple, serial No SRC 6040. Manufactured by Tagliabue Instrument Division, Western Electric Instrument Corporation, Newark, N. J. Used to record and control the temperature of the Veritemp combustion furnace.

Standard Cell. One, Eplab. Manufactured by Epperly Laboratory, Inc., Newport, R. I. Used as a reference cell for the potentiometer.

Valve, Reducing. One, carbon dioxide, compressed gas regulator. Obtained from Mathison Company, East Rutherford, N. J. Used to reduce and control carbon dioxide gas pressure to the test apparatus.

Valve, Reducing. One, compressed gas regulator, model VTS 201. Manufactured by Victor Equipment Company, Los Angeles, Calif. Used to reduce and control helium gas pressure to the test apparatus.

Variac. One, 20 amp, 270 v, 7 KVA, type 50-B. Manufactured by General Radio Company, Cambridge, Mass. Used to control the current flow to the Hoskins electric furnace.

X-Ray Diffraction Machine. One, and components, type S3000-2, serial No 277. Manufactured by General Electric Company, Pittsburgh, Pa. Used to determine the corrosion products' composition.

ABSTRACT

CORROSION BY MOLTEN MIXTURES OF SODIUM CARBONATE
AND VANADIUM PENTOXIDE

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The problem of corrosion of steels by slags deposited during combustion of heavy petroleum fuels which contain sodium and vanadium becomes very severe when the temperature of the metal exceeds 550 to 600 °C, thus placing undesirable limitations on both the manufacturers and users of heavy fuel oil fired boilers and turbines. To contribute to the understanding of this problem, this study was made to determine the mechanism of the reaction between iron and molten mixtures of sodium and vanadium oxides.

Tests were conducted on 1020 carbon steel in carbon dioxide and helium atmospheres at temperatures from 593 °C to 927 °C using a slag composed of 64 mole per cent vanadium pentoxide-36 mole per cent sodium

carbonate, and at 927 °C using sodium-vanadium slags with 100, 90, 50, 36, and 16 mole per cent sodium carbonate. Tests were also made with Hastelloy B, Hastelloy X. and 347 stainless steel. The metal specimens were coated with the slag, heated at a constant temperature in a combustion furnace for up to 36 hours, and cleaned and weighed to determine weight loss. The slag and corrosion products were analyzed by x-ray diffraction techniques.

The 64 mole per cent vanadium pentoxide slag was chosen for the most extensive study since it represents the primary eutectic of the sodium oxide-vanadium pentoxide system and favors the formation of the complex sodium vanadyl vanadate, $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$, considered by many investigators to be the major cause of corrosion.

This work showed that the corrosion reaction results from the oxidation of iron by vanadium oxides, with the reaction proceeding as follows: (1) oxidation of iron to ferrous oxide with reduction of vanadium pentoxide to the tetroxide, (2) fluxing of the initial products of corrosion by the slag, and (3) simultaneous additional oxidation of iron and further oxidation of ferrous oxide to ferrosiferrous and ferric oxide. At

intermediate temperatures, 670 °C, step (2) controls the corrosion rate for a portion of the reaction, as evidenced by two very distinct changes in slope of the weight loss-time curve. At higher temperatures, 927 °C, no distinct changes in slope were observed.

Tests at various slag compositions show that the effect of carbon dioxide increases as the sodium carbonate concentration of the slag increases. Above a one to one mole ratio, increasing the vanadium pentoxide content of the slag increases the rate of corrosion. At 50 mole per cent vanadium pentoxide the rate of corrosion of 1020 carbon steel was approximately 17 milligrams per square inch, hour, while at 84 mole per cent vanadium pentoxide the rate was 65 milligrams per square inch, hour.

The tests conducted with alloy steels show that increasing the nickel content of the alloy from 12.5 to 61.0 per cent, increases the corrosion rate from 1.7 to 10.0 milligrams per square inch, hour.