*Materials Science and Engineering*
American Society for Metals, Metals Park, Ohio, and Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands

**Invited Review**

# Accelerated Oxidation of Ferrous Materials in $CO_2/CO$ Gas Mixtures

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(Received December 28, 1971)

CONTENTS

## *Summary*

*The extremely sluggish oxidation of scrap steel can be substantially accelerated by pretreating the charge in an aqueous solution or suspension of the sodium salt of certain oxyacids. A requirement is that the acid anhydride possess a low melting point. Hence, $V_2O_5$, $MoO_3$, $PbO$, $Bi_2O_3$ and $Sb_2O_3$, as present in solutions of vanadate, molybdate, plumbite, bismuthite and antimonite, respectively, are suitable accelerators. Oxidation acceleration with bismuthite and antimonite increases with both concentration of the accelerator and pretreatment time, suggesting a hydrolytic displacement reaction by which the promoter oxide is impregnated on the steel surface. The accelerated oxidation curve of various steels remains essentially the same despite wide variabilities in the kinetic curves of untreated steel batches. The degree of oxidation acceleration is inversely correlated with the melting point of the oxide promoter.*

## I. INTRODUCTION

The oxidation of iron has been investigated for many years[1]. From a technological point of view, these studies have concentrated on controlling oxidation, and thus corrosion, of the metal. The objectives of research in this paper are diametrically opposite, namely, to provoke the oxidation reaction in steels.

The process of reduction roasting of iron ores with metallic iron was described[2] as a means of converting the extensive nonmagnetic reserves of submarginal iron ores to magnetic usable products by partial reduction. Scrap iron, which is being accumulated in alarming quantities, could be effectively used as a reductant, thereby simultaneously upgrading the nonmagnetic taconite ores and affording a means of combating the ever-growing problem of scrap solid waste disposal. Speeding up the oxidation of steel is, therefore, investigated as a means of increasing the efficiency of this process. Metallurgical reduction processes utilizing the iron in the scrap steel, exemplified by the extraction of copper[3] from its oxide concentrates, would also be improved by the techniques developed in this paper.

### *A. Oxidation of iron during reduction roasting of ore*

The reduction roasting of iron ore with metallic iron can be ideally represented by the following cyclic process, in which magnetite is assumed to form from both metallic iron and the hematite ore:

$$\begin{tikzcd}
3\,Fe+4\,CO_2 \arrow[r, "k_1"] & Fe_3O_4+4\,CO \arrow[d, "(4H_2)"] \\
8\,Fe_3O_4+4\,CO_2 \arrow[u, "(4H_2O)"] & 12\,Fe_2O_3+4\,CO \arrow[l, "k_2"']
\end{tikzcd}$$

The reduction reaction, with rate coefficient $k_2$, has been extensively investigated and is, in general, much faster than the sluggish tarnish reaction, with rate coefficient $k_1$. In the temperature range of 900° to 1,000°C, wustite (FeO) can be 50% reduced to metallic iron in about 7 minutes[4], whereas iron in scrap steel is only 3% oxidized to magnetite[5] (or 4% oxidized to wustite) in about 70 minutes. Thus with commercial charges, the reduction rate is more than two orders of magnitude (500/4) faster than the oxidation rate. Wustite rather than magnetite reactions are chosen in this example because the former are slower and hence constitute the rate-determining steps for the overall iron oxidation–reduction processes. The primary objective of this investigation was to find means to increase $k_1$ to the level of $k_2$ and thereby increase the rate at which the above cyclic process occurs. An ideal situation should utilize the oxygen-carrying gases $CO_2$ and CO both as oxidants and as reductants, in a manner to simulate the oxidation–reduction roasting cycle, and maximize the extent of magnetic formation.

The oxides of iron possess a higher molar volume than the parent metal; hence, they can form a compact layer around the metal that is impervious to gas flow. Ionic or atomic diffusion through the oxide layer is therefore important to sustain the oxidation reaction. This is exactly the reverse of the situation involved in iron oxide reduction. In this process the iron layer formed around the oxide particles is very porous owing to its smaller molar volume; according to the rule of Pilling and Bedworth[6], it is non-protective, and allows the reducing gas to diffuse freely to the reaction interface. Because gaseous diffusion through pores is faster than atomic diffusion through solids, the reduction of iron oxides is usually faster than iron oxidation.

It appears that the most logical method of enhancing the rate of oxidation would be to accelerate the process of atomic or ionic diffusion through the solid adherent oxide phase. Because nothing can be done to change the nature of the diffusing species, attempts should be made to modify the properties of the diffusion medium itself. Oxides with relatively low melting points would be expected to increase the fluidity and plasticity of the diffusion medium and hence increase the rate of ionic diffusion. Diffusion in liquids is known to be several orders of magnitude faster than diffusion through solids.

### *B. Catastrophic oxidation of iron alloys*

Leslie and Fontana[7] were the first to report that excessively fast oxidation and disintegration of some alloys may occur when the alloying component forms a low-melting oxide. They referred to this phenomenon as catastrophic oxidation. Important examples of catastrophic oxidation were found in oxidation of metals and alloys in the presence of molybdenum and vanadium. Rathenau and Meijering[8] pointed out the importance of liquid oxide phases in catastrophic oxidation. They found that the accelerated attack became important at the eutectic temperatures of the binary or ternary oxides involved. For the chromium-containing alloys, the onset of catastrophic oxidation occurred at about the temperature at which liquid molybdenum oxide dissolves $Cr_2O_3$.

The detailed mechanism of this type of accelerated attack has not been elucidated. Liquid phases are probably initially formed on the oxide surface in the presence of the accelerator. It appears, however, from various studies[7,8], that the rapid oxidation takes place at the scale–alloy interface. It has been hypothesized that the liquid phases penetrate the scale along grain boundaries to the alloy surface where the rapid oxidation takes place[8]. Liquid phases along grain boundaries may also serve as rapid diffusion paths for the reacting ions, causing accelerated attack. Catastrophic oxidation in alloys for which alloying additions form low-melting oxides has been studied for molybdenum-containing alloys[9].

In this research, the phenomena of catastrophic oxidation are investigated from a different approach. Instead of alloying the metal (iron) with the accelerating material, the steel surface was impregnated by treating in an aqueous solution or suspension of the sodium salt of the oxyacid containing the promoter. Pretreatment in either sodium metavanadate, sodium molybdate, sodium plumbite, sodium bismuthite or sodium antimonite served as a means of surface impregnation of scrap steel with minute amounts of the promoter.

In a previous communication[5] from this laboratory, it was shown that surface impregnation of steel strips with small quantities of the oxides of vanadium(V), molybdenum(VI), and lead(II) increased their rate of oxidation in carbon dioxide atmospheres

In contrast with the pentavalent vanadium in the metavanadate, the tetravalent state in vanadyl sulfate did not accelerate oxidation. X-Ray fluorescence examination of the pretreated steel strips indicated the presence of small quantities of the accelerator on the surface layer.

Steel pretreatment in aqueous solutions of sodium carbonate[5] of the same pH as that of the accelerator solution did not change the oxidation rate. Hence, neither sodium ions nor solution alkalinity were responsible for the observed results. The accelerating effect was explained on the basis of the hydrolytic decomposition of the oxyanion containing the promoter with subsequent slow interaction with the metal surface, coupled with the tendency of vanadate and molybdate to form polyanions. A minimum in the oxidation speed was observed[5] at intermediate vanadate concentrations. This was explained on the basis of vanadate polymerization to form polyanions whose proportion increased with increasing vanadium concentration. Consideration of interspecies equilibria indicated that the concentration of vanadate monomer, and hence the quantity of the accelerator, $V_2O_5$, will exhibit a minimum value at some intermediate concentration of the metavanadate bath.

The present paper extends the work in reference 5 to two newly discovered promoters, sodium bismuthite and sodium antimonite.

## II. EXPERIMENTAL WORK

### *A. Materials and apparatus*

The oxidizable charge consisted of seven steel strips, each 7 by 2 by 0.1 cm, cut from new, unpainted automobile parts. An average charge weighed from 64 to 66 g and possessed a geometric surface area of about 209 cm$^2$. Colorimetric and volumetric analyses of the minor constituents in a random sample showed the presence of Ni, Mn, Cr, Cu, C, Si and P in the percentages of 0.60, 0.13, 0.05, 0.037, 0.25, 0.01 and 0.003, respectively. Commercially available carbon dioxide (Cardox)*, carbon monoxide (Matheson C.P) and nitrogen (National Cylinder Gas Co.) were respectively 99.96, 99.5 and 99.99 percent minimum purity. Low-carbon deep-drawing automobile steel from fender skirts and hoods was kindly supplied by the Ford Motor Co., St. Paul, Minn. Chemically pure sodium metavanadate, sodium molybdate, lead nitrate, bismuth nitrate, antimony chloride and sodium hydroxide were all products of Fisher Scientific Co. Preparation of sodium bismuthite or sodium antimonite from bismuth nitrate or antimony chloride, respectively, was accomplished by quatitatively precipitating the promotor's hydroxide and adding the excess stoichiometric quantity of sodium hydroxide required to form the salt. For example, 10% sodium bismuthite, $NaBiO_2$, was prepared by dissolving 18.37 grams bismuth nitrate pentahydrate in 50 ml distilled water. The solution was then slowly poured into a beaker containing 22.24 ml of 6.25 *N* sodium hydroxide, while the mixture was vigorously mixed with a magnetic stirrer. The mixture was then diluted to 100 ml with distilled water and stored.

Oxidation curves were measured gravimetrically by a displacement transducer balance whose output allowed the weight-gain of the oxidizable sample to be continuously recorded on a strip chart. The charge was placed in a Vycor crucible having a Vycor gas delivery tube and a quartz cover. The temperature of the sample was measured by a Pt *versus* Pt–10% Rh thermocouple placed in a Vycor protection tube adjacent to the sample strips. The sample temperature was monitored on another strip chart during the progress of oxidation. Maximum deviation in this temperature did not exceed $\pm 2$ deg C for an average temperature of 900°C, which was the oxidation temperature used throughout this work.

### *B. Procedure*

Grease and oil were removed from the steel strips by washing in a warm detergent solution, then in warm water, followed by acetone and methanol, and finally air-drying.

Surface impregnation of steel with the accelerator was effected by immersing the preweighed clean strips in an aqueous bath of the pretreatment agent at room temperature for a prescribed time. The weight of the pretreated charge, after air-drying, was determined immediately prior to the oxidation test, and was generally about 50 mg more than the weight before immersion for an average charge of 65 g.

The strips were then placed in the Vycor crucible and separated by 3/8-inch alumina beads. Oxidation was conducted with 85% $CO_2$ and 15% CO at a flow rate of 4 liters (STP) per minute. According to the Fe–O–C phase diagram, the oxidation potential of this mixture is thermodynamically capable of forming magnetite from iron at 900°C.

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* Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

The final weight of the charge was also determined at the end of the test by a Sartorius analytical balance. The agreement between the final weight gain in oxygen and the weight gain recorded by the displacement transducer was always excellent, with a difference not exceeding 1%. Percent oxidation was calculated on the basis of the original steel weight prior to the pretreatment and on the assumption that full oxidation was achieved when the iron content of the sample was transformed to magnetite. The weight gain per unit initial geometrical surface area of the steel was also calculated to investigate the oxidation kinetics.

## III. RESULTS AND DISCUSSION

Research described in this paper extends previous investigations[5] of accelerated steel oxidation with vanadium, molybdenum and lead to include the bismuth and antimony accelerators.

### *A. Pretreatment in bismuthite solutions*

Oxidation acceleration with bismuth oxide was tested by pretreating the scrap steel for one hour in 10% sodium bismuthite solution. Similar to previous results with plumbite, vanadate and molybdate solution, a spectacular oxidation acceleration was clearly demonstrated on comparing oxidation curve b in Fig. 1 with the blank test of untreated steel shown in curve a of the same Figure. The bismuthite-treated steel was 50% oxidized at 200 minutes, whereas the untreated scrap was only 15% oxidized in the same time period. The initial oxidation rate as determined by the slope of curve b was almost nine times that of the untreated steel.

The effect of the accelerator concentration on the magnitude of steel oxidation acceleration is illustrated by curves b, c, d and e of Fig. 1, where the percentage of bismuthite in the treating solution dropped from 10 to 5, 1 and 0.1, respectively. As expected, lower concentrations of the accelerator resulted in lower magnitudes of oxidation acceleration. The hydrolytic decomposition of sodium bismuthite is believed to deposit a thin layer of bismuth trioxide on the steel surface, thus

$$2\,NaBiO_2 + 4\,H_2O \rightarrow 2\,NaOH + 2\,Bi(OH)_3$$
$$3\,H_2O + Bi_2O_3 \hookleftarrow$$

The deposited layer of bismuth trioxide is evidently responsible for accelerating the oxidation reaction.

By contrast, pretreatment of scrap steel in a 10% bismuth nitrate solution did not produce any noticeable effect on the oxidation curve. This is because in such solutions, the iron of the steel would displace the nobler bismuth, thus

$$Bi(NO_3)_3 + Fe^\circ \rightarrow Fe(NO_3)_3 + Bi^\circ\,.$$

The standard electrode potentials at 25°C for the $Fe/Fe^{3+}$ and $Bi/Bi^{3+}$ couples are 0.04 and $-0.20$ volt, respectively. Visual examination of the surface layer of steel strips treated in bismuth nitrate solutions indicated the presence of a loosely adhering reddish-brown layer of metallic bismuth. A surface layer of bismuth atoms on the steel strips does not appear to promote the oxidation of iron because iron will be preferentially oxidized. Bismuth oxide formation is therefore a prerequisite for oxidation acceleration.

### *B. Pretreatment in antimonite solutions*

Surface impregnation of scrap steel with antimony oxide, $Sb_2O_3$, also accelerated its rate of oxidation. The choice of antimony oxide (melting point = 656° C) was based on previous experience on oxidation acceleration with $V_2O_5$, $MoO_3$, PbO and $Bi_2O_3$. To introduce the accelerator, the oxidizable charge was pretreated in an aqueous suspension of 10% sodium antimonite, $NaSbO_2$, for one hour at room temperature. The kinetic curve for the oxidation of this pretreated steel at 900°C is shown as curve b in Fig. 2. Curve a shows the oxidation of an untreated batch of the steel. When the oxidizable charge was instantly pretreated (about 10 seconds) in 0.71 molar aqueous sodium antimonite (12.55%), curve c of Fig. 2 resulted.

Oxidation acceleration with $Sb_2O_3$ increased with both the concentration of the accelerator and the pretreatment time. The effect of immersion time in 0.71 molar sodium antimonite from 10 seconds to 6 hours on the oxidation kinetics of scrap steel is clearly demonstrated by the data in Fig. 3. No significant gain in oxidation acceleration was realized by prolonging the pretreatment time beyond two hours. At 200 minutes, the oxygen uptake per $cm^2$ of steel was 48.2 and 53.3 milligrams after pretreatment in 10% and 12.55% sodium antimonite, respectively. These values are to be compared with the 12.0-milligram oxygen uptake obtained with untreated steel in the same time period.

### *C. Effect of steel origin on its accelerated oxidation*

During the progress of this research, different scrap steel batches were necessarily used. The first

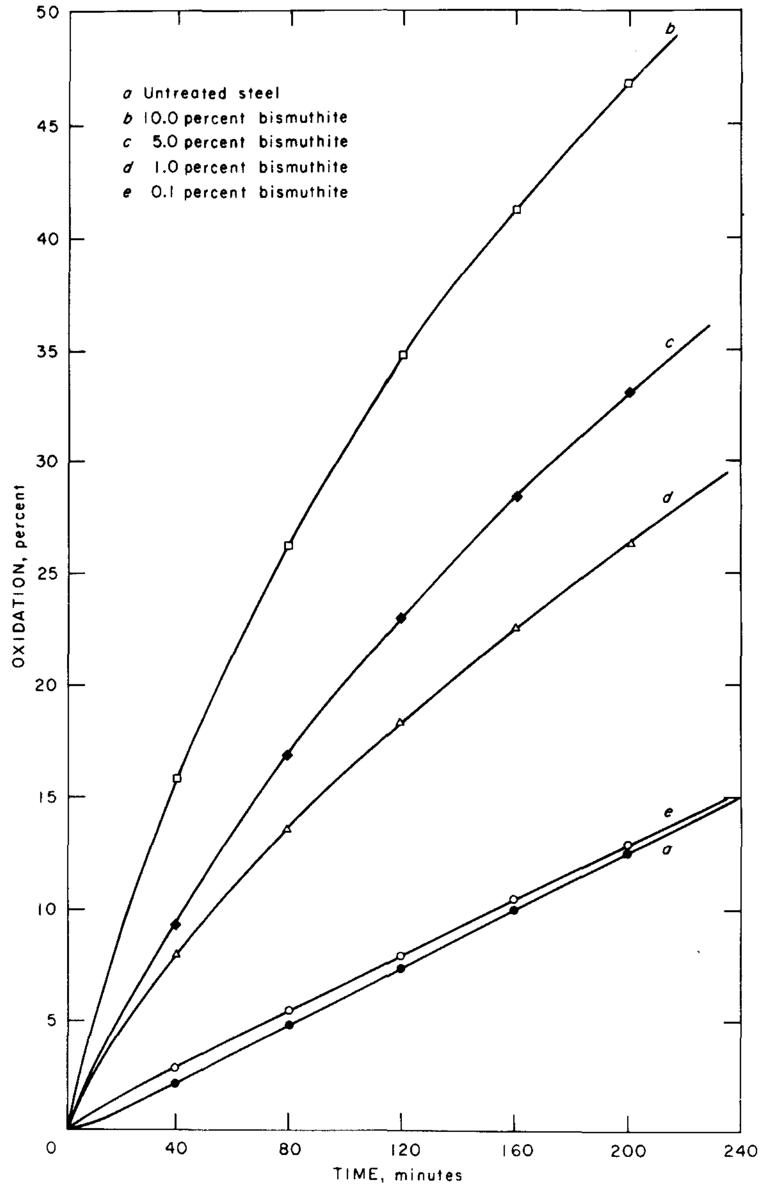

Fig. 1. Effect of one-hour pretreatment in sodium bismuthite on the oxidation kinetics of scrap steel.

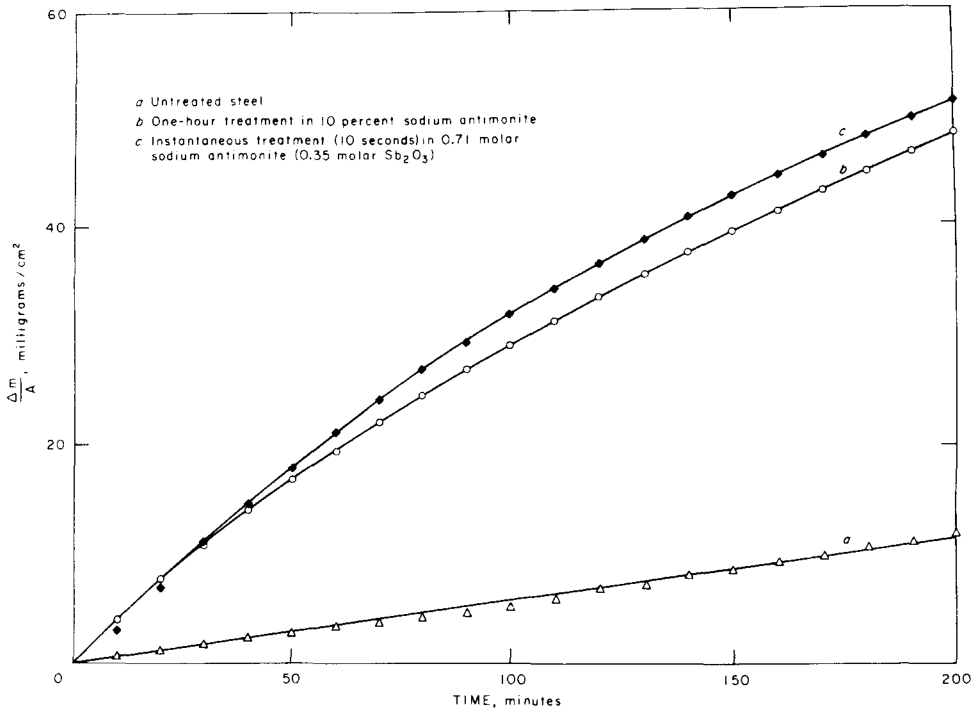

Fig. 2. Effect of steel pretreatment in sodium antimonite on its oxidation kinetics at 900°C.

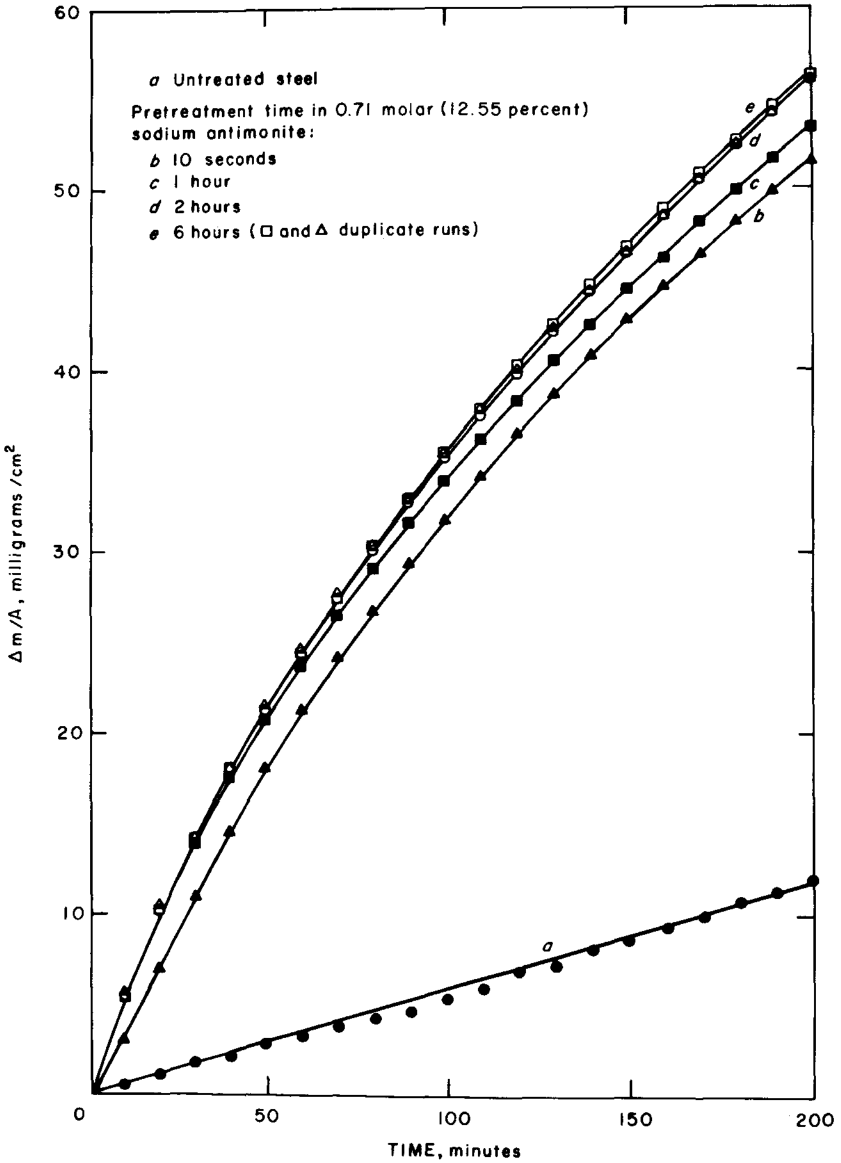

Fig. 3. Effect of pretreatment time in 0.71-molar sodium antimonite on the oxidation of scrap steel.

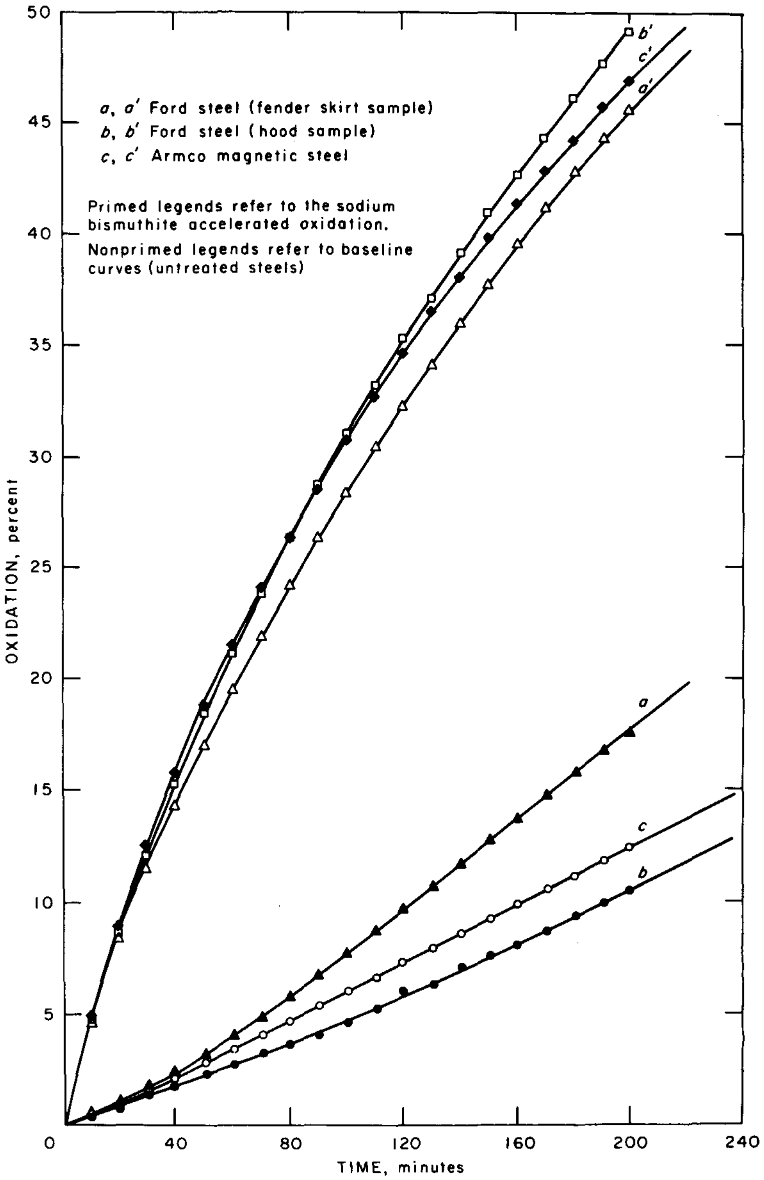

Fig. 4. Effect of steel batch origin on its baseline and accelerated oxidation at 900°C.

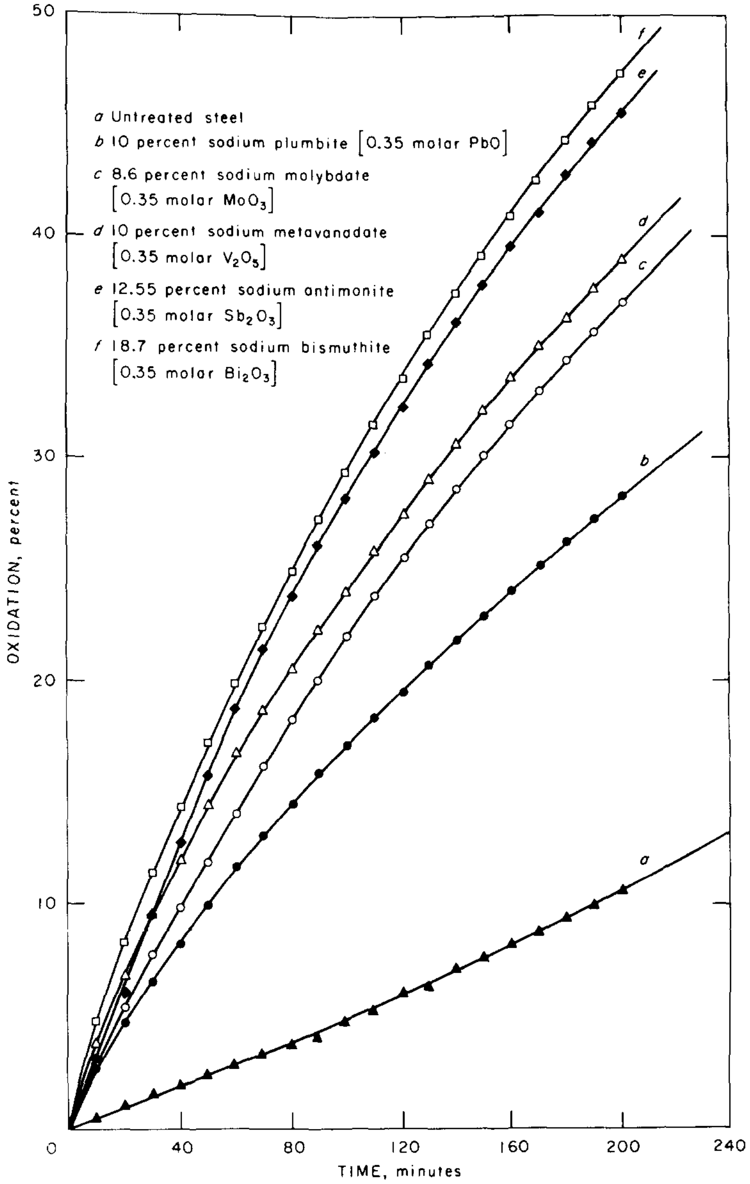

Fig. 5. Accelerated oxidation of scrap steel by pretreatment with various reagents.

TABLE I

Effect of melting point of the oxide promotor on steel oxidation acceleration

| *Accelerator bath* | | *Sodium metavanadate* $NaVO_3$ | *Sodium molybdate* $Na_2MoO_4$ | *Sodium plumbite* $Na_2PbO_2$ | *Sodium antimonite* $NaSbO_2$ | *Sodium bismuthite* $NaBiO_2$ |
|---|---|---|---|---|---|---|
| Oxide promotor | | $V_2O_5$ | $MoO_3$ | PbO | $Sb_2O_3$ | $Bi_2O_3$ |
| Concentration | percent | 10 | 8.6 | 10 | 12.6 | 18.7 |
| Concentration | molar | 0.71 | 0.35 | 0.35 | 0.71 | 0.71 |
| Concentration of promotor | molar | 0.35 | 0.35 | 0.35 | 0.35 | 0.35 |
| Steel oxidation at 200 min | percent | 38.9 | 26.9 | 28.4 | 45.4 | 46.9 |
| Melting point of oxide promotor | °C | 690 | 795 | 888 | 656 | 860 |

Ford steel batch from fender skirt pieces was used in previous experiments[5] with vanadium, molybdenum and lead accelerators. Their baseline oxidation is shown as curve a, Fig. 4. The present experiments with bismuth and antimony accelerators were conducted on Ford steel (1971 hood samples); the baseline oxidation is shown in curve b, Fig. 4. Despite the significant variabilities in the baseline, the bismuthite-accelerated oxidation for the two steel batches did not change remarkably, as shown in curves a′ and b′, Fig. 4. To further validate this conclusion, a third batch of steel obtained from Armco Steel Corporation (designated as Armco magnetic steel) was used, and its baseline oxidation is shown as curve c, Fig. 4. Upon subjecting this steel to a one-hour pretreatment in 10% sodium bismuthite, its oxidation was accelerated to curve c′, Fig. 4. The variability in the oxidation curves of the pretreated steels is much less than that of the untreated steel. It appears, therefore, that the accelerated oxidation of steel is not very dependent on the origin of the steel.

Changes in the alloying elements in the various steels are undoubtedly responsible for the variability in their baseline oxidation curve. The presence of the oxidation promoter with its low melting point will ostensibly override the effects of the minor elements in steel. The melting point and plasticity of the scaling layer will be most affected by the oxide of the lowest melting point in the eutectic mixture. This finding was gratifying because it obviated the need for test normalization to draw conclusions, or the repetition of a subseries set of tests because of changes in the baseline of the steel batch.

### *D. Dependence of accelerated oxidation on the promoter's melting point*

Previous results[5] indicated a systematic inverse dependence between the magnitude of oxidation acceleration and the pretreatment time in vanadate or molybdate baths. Contrary to expectation, steels that were momentarily dipped in these baths oxidized at a much faster rate than those pretreated for longer time periods. These findings were explained[5] by the gradual reduction of pentavalent vanadium or hexavalent molybdenum by iron of the steel to produce lower valency species which have no enhancing effect on oxidation. This was also substantiated by perceptible color changes in the vanadate bath from colorless to yellowish, brownish and finally violet-green with the progress of the steel pretreatment. These anomalies were absent with plumbite, bismuthite and antimonite baths, and hence the accelerated oxidation with these increased with pretreatment time.

In order to correlate the magnitude of oxidation acceleration with the melting point of the oxide promoter, the present results should be compared with those previously reported[5] with other accelerators at the same molar concentration and with a common pretreatment time. In order to incorporate the data with molybdate and vanadate, comparison must be made using the method of instantaneous dipping (10 seconds) in the accelerator bath. Tests were therefore conducted in which the oxidizable charge was momentarily pretreated with 18.7% sodium bismuthite and 12.6% sodium antimonite (0.71 molar solutions). The resulting oxidation data at 900°C are shown in curves e and f of Fig. 5 for the antimonite- and bismuthite-treated steels, respectively. Table 1 contains these new data, plus additional data that were reported in a previous paper[5]. The melting points of the oxide promoters[10] are given in the last row of this table. Thus, with solutions that are equimolar with respect to the promoter oxide, the degree of steel oxidation acceleration increases in the following sequence: lead, molybdenum, vanadium, antimony and bismuth. Except for bismuth, this is also the sequence of decreasing melting points of their respective oxides.

Three bismuth trioxide varieties are reported in reference 10: the yellow rhombic melts at 820°C, the gray cubic melts at 704°C and the whitish-yellow melts at 860°C. Dark-red bismuth pentoxide, $Bi_2O_5$, loses oxygen at 150°C, while the brown bismuth tetroxide, $Bi_2O_4 \cdot 2H_2O$, loses water at 180°C. It appears that the oxide deposited from sodium bismuthite solutions is a mixture of oxides, hence it was necessary to measure the melting point of the freshly precipitated oxide. The melting point* was determined in air in a Vycor crucible, using a chromel-alumel thermocouple. Only Vycor contacted the sample. The sample was found to melt with decomposition at 653° to 655° ± 5°C. The red-brown melt evolved bubbles of gas and gradually converted to a two-phase system consisting of colorless liquid and a yellow solid. No freezing point could be determined because of the decomposition after melting. The average melting point of the bismuth oxide accelerator was therefore taken as 654° ± 5°C.

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* The authors are indebted to Prof. Lawrence E. Conroy, School of Chemistry, University of Minnesota, for determining the melting point of the bismuth oxide sample.

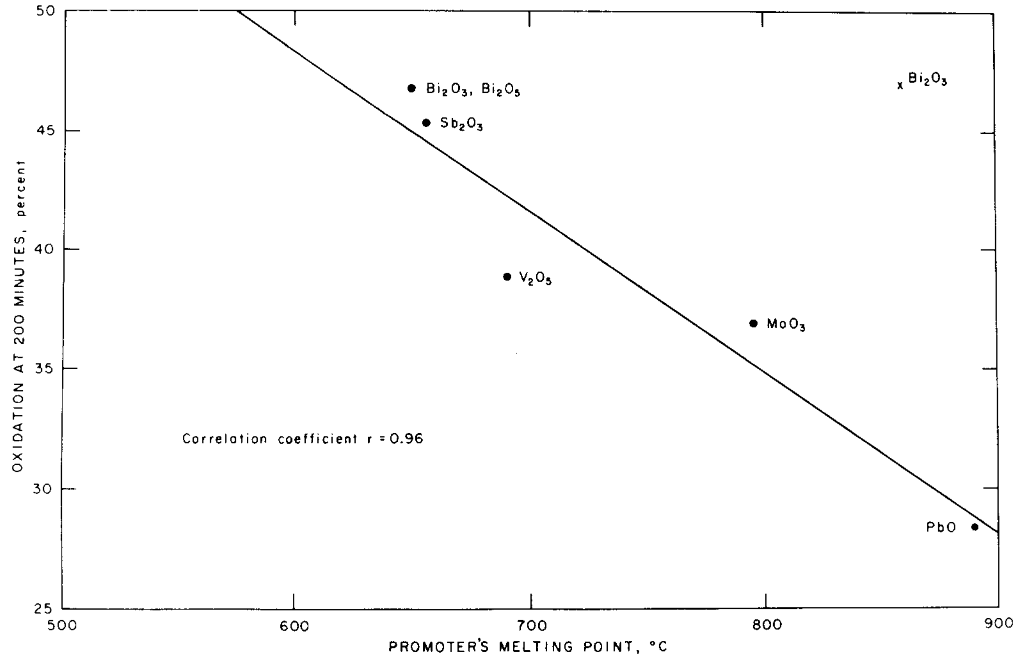

Fig. 6. Variation of the extent of oxidation at 200 minutes with the melting point of the oxide promoter.

When the percent steel oxidation achieved at 200 minutes was plotted against the melting point of the oxide promoter, a straight line with a simple correlation coefficient of 0.96 was obtained as shown in Fig. 6. Point x in that Figure refers to the bismuth accelerator as if it were the simple trioxide, while the bismuth point close to the line in Fig. 6 refers to a mixture of bismuth oxides, $Bi_2O_3$ and $Bi_2O_5$, referred to as $Bi_2O_4$. Barring complications from chemical changes in the accelerator bath, an inverse correlation appears to exist between the accelerated oxidation of scrap steel and the melting point of the oxide promoter.

## IV. CONCLUSIONS

The oxidation of scrap steels in $CO_2$/CO gas mixtures can be appreciably promoted by surface impregnation of the steels with small quantities of the oxides of antimony (III) and bismuth (III and V). The interaction between iron of the steel and the accelerator in the bath leads to deposition of the oxide promoter on the steel surface in quantities sufficient to induce catastrophic oxidation. The accelerated oxidation is virtually independent of the nature of the original steel batch. A significant correlation exists between the degree of oxidation acceleration and the melting point of the oxide promoter. The results demonstrate that scrap steels can be catastrophically oxidized without need for prior alloying with vanadium, molybdenum, lead, antimony or bismuth.

## ACKNOWLEDGEMENTS

The authors are grateful to Dr. T. A. Henrie, Deputy Director, U.S. Bureau of Mines, Department of the Interior, for suggesting and permitting publication of the material in this paper.

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