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THE EFFECT OF SMELT/GAS INTERACTION ON SA-210 CARBON STEEL CORROSION

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ABSTRACT

Coupon tests of SA-210 carbon steel were carried out using a 1% H₂S gas environment with or without smelt. Three smelt compositions, with different percentage of Na₂CO₃, Na₂SO₄, and Na₂S, were used in the study. Increase in weight loss (25%) was recorded in tests using smelt #1 (80% Na₂CO₃, 12% Na₂SO₄, 8% Na₂S), while smelt #2 (65% Na₂CO₃, 15% Na₂SO₄, 20% Na₂S) decreased the weight loss (9%) in 24-hour tests compared to similar tests carried out in 1% H₂S gas mixture without smelt. The smelts developed a crust with yellow color. The addition of 1% O₂ to the 1% H₂S gas environment increased the weight loss of SA-210 carbon steel by 83% and 170% in 4- and 24-hour tests, respectively, compared to similar tests carried out in only 1% H₂S gas environment. The addition of 2-4% of NaCl to the smelt, in a 1% O₂ + 1% H₂S environment, did not significantly change the weight loss. The smelt developed a strong crust with orange color. Whereas, using only NaCl, the weight loss increased by 218%.

INTRODUCTION

One of the highest rates of corrosion in the recovery boilers occurs on the fireside of water wall tubes in the lower furnace area. This area is generally under reducing conditions. Smelt, a frozen mixture of salts, accumulates on the furnace tubes and reduces the water wall tube temperature and thus reduces the metal wastage. The corrosion product of water wall tube in the lower furnace is mainly iron sulfide on carbon steel and chromium sulfide on the stainless steel. For the corrosion reactions to continue on the tubes of kraft recovery boiler, the bulk gases from the furnace must pass through the frozen smelt on the tube and react with tube material, as is shown schematically in Figure 1. This interaction might produce mixture of gases with concentrations different from the bulk gas mixture. Sulfide scale on the tube surface grows by the reaction of the resultant gas mixture with the tube material at the scale/smelt interface. The interaction of the bulk gas mixture with the smelt components is an important step in the water wall tube corrosion in the lower furnace area. Most of the tests carried out earlier were done by dipping test coupons in the smelt [1-3]. Stelling and Vegeby [1] tested carbon steel in 0.1% H₂S, 0.09% O₂, 10% H₂, 3.5% H₂O, bal. N₂ at 375°C and found the weight loss of 0.37 mg/cm²·hr. When the same test was repeated with test coupons dipped in smelt 75% Na₂CO₃ and 25% Na₂S·3H₂O, the weight loss was 0.12 mg/cm²·hr. It was concluded that the smelt acted protectively against gaseous corrosion. As the Na₂S·3H₂O percentage increased, the weight loss increased to 0.18 mg/cm²·hr at 40% Na₂S·3H₂O. Plumley, et al. [3], studied the effect of the smelt constituents individually on carbon steel at 371°C in nitrogen gas and found that the weight loss increased by 20% in Na₂CO₃ but decreased by 11% in both Na₂SO₄ and Na₂S. Tests were also done in air and Plumley, et al. [3], reported that the tests carried out in the presence of Na₂CO₃ and Na₂SO₄ showed the same degree of weight loss, whereas tests in Na₂S showed a fourfold increase in weight loss. That led them to suggest that some oxidation product of Na₂S is the reactive substance and not Na₂S itself. Furthermore, Na₂S₂O₃ in nitrogen produced 300% increase in weight loss compared with that of Na₂S in air. Fonder and Ahlers [3] tested C1018 carbon steel in gas mixture (1% H₂S, 1% O₂, 10% CO₂, 2% H₂O, bal. N₂), where specimens were dipped in synthetic smelt (80% Na₂CO₃, 12% Na₂SO₄, and 8% Na₂S), at 400°C and found weight loss of 0.032 mg/cm²·hr in a 5 hour test. The 5% addition of each Na₂S₂O₇, Na₂S₂O₃, and NaCl to the base smelt composition increased the weight loss by 15%, 54%, and 57%, respectively.

EXPERIMENTAL PROCEDURE

SA-210 carbon steel specimens were cut from 5-cm-OD tube and burnished according to the standard procedure described in AF&PA/95 report [4-5]. The chemical composition of SA-210 carbon steel alloy is given in Table I. The specimen dimensions were 2.5 cm x 1.8 cm x 0.5 cm. Coupons were cleaned with acetone and weighed before they were hanged on a glass tree and placed in the reaction tube. Smelts were prepared by mixing their constituents

for at least six hours in an enclosed bottle, making sure that the constituents were not exposed to air during this procedure. Smelt was loaded in 300-mL, 304 stainless steel cylinder. The original gas mixture (1% H₂S + N₂) was passed through the smelt and the resultant gas mixture was taken to the reaction tube where the coupons were exposed to this mixture. A schematic drawing of the experimental apparatus is shown in Figure 2. The temperature of the smelt cylinder was controlled to $\pm 5^{\circ}\text{C}$ of the test temperature at which the test coupons were exposed in the reaction tube. After the test was finished, specimens were taken out of the reaction tubes, sulfide scale was removed by sandblast and the specimens were weighed to an accuracy of 0.1 mg. The smelt compositions used in these tests are shown in Table II.

RESULTS

Smelt Experiments

Two sets of tests with either 25 or 50 g of smelt #1 were carried out at 400°C for three time periods (4, 8, 24 hr). Two specimens were tested for each test conditions. The change in weight loss of SA-210 is shown in Figure 3. The weight loss of SA-210 in 1% H₂S is 0.8 mg/cm² and 1.4 mg/cm², respectively, for the tests carried out for 4- and 24-hours. That gave a corrosion rate of 0.03 mg/cm².hr. Using 25 g of smelt, the weight loss increased by 12%, 13%, and 8% for 4-, 8-, and 24-hour tests, respectively, when compared with similar tests done in 1% H₂S gas environment. Testing 50 g of smelt #1 resulted into an increase in the weight loss of 25%, 4%, and 26% respectively, for 4, 8, and 24-hour test, respectively. Furthermore, using two cylinders to load 50-g weight of smelt (25 g in each cylinder), the weight loss increased by 29% and 2% in 8- and 24-hour tests, respectively, compared to similar tests without smelt. A larger amount of smelt was not tested for concerns that it might affect or block the gas flow. The scale was removed mechanically (low-pressure sandblast) to calculate the weight loss. Using 50-g weight of smelt #2 in 4- and 24- hour tests decreased the weight loss by 28% and 9% compared with tests in only 1% H₂S. Smelt #3 increased the weight loss by 4% and 11% in the same time interval, as is shown in Figure 4.

Effect of Sodium Chloride

Tests were also done to study the effects of chlorides in a recovery boiler environment due to introduction of chloride rich effluents in the recovery cycle. Tests were carried out in the presence of smelt #4-6, which are smelts #2-3 with 2% or 4% of NaCl. Smelt compositions are given in Table II. The use of 50 g of smelt #4 decreased the weight loss by 46% and 15% in 4- and 24-hour tests, respectively, when compared with similar tests done in 1% H₂S gas only. Whereas, tests using 50 g of smelt #5 showed a decrease in the weight loss by 19% and 24% in the same time periods.

Effect of Oxygen

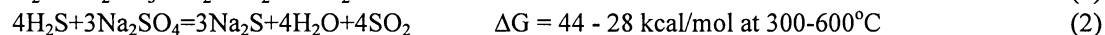
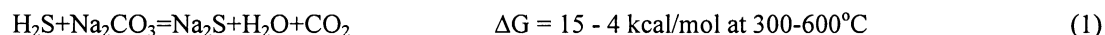
Thermodynamic calculations suggest that NaCl may greatly influence the weight loss in the presence of oxygen gas. Oxygen gas is known to increase the weight loss to a maximum at approximately a 1:1 ratio with H₂S. The addition of 1% O₂ to 1% H₂S gas increased the weight loss to 1.43 mg/cm² in 4-hour and 3.8 mg/cm² in 24-hour test, which corresponds to 0.0985 mg/cm².hr. That means that the addition of 1% O₂ to the gas mixture increased the weight loss by 83% and 170% in 4- and 24-hour tests, respectively, when compared with similar tests in 1% H₂S gas only, as is shown in Figure 5. Thermodynamic calculations suggested that the addition of oxygen to H₂S pushed the reaction towards higher elemental sulfur production from H₂S gas. Using 50 g of smelt #6 in 1% O₂ + 1% H₂S decreased the weight loss by 17 and 48%, when compared with similar tests without smelt in the same time periods, as is shown in Figure 6. The effect of NaCl here is not very clear, which may be because of its low concentration in the smelt. However, tests with 50 g of smelt #7 increased the weight loss for 24-hour-time period to 135% and 300% in two different tests. Gas flow was blocked in the later tests due to sulfur condensation in the cold areas of the tube. Repeating the same tests with 10, 30, 50 g of NaCl increased the weight loss by 218%, 135%, and 136%, respectively, as shown in Figure 6.

DISCUSSION

Smelt Experiments

Assuming that hydrogen sulfide reacts with smelt components individually, thermodynamic calculations indicate

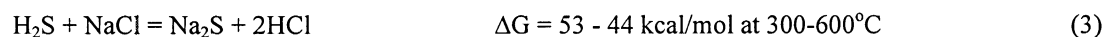
that the reaction of Na_2CO_3 with H_2S to produce Na_2S , H_2O , and CO_2 has a positive free energy. Similarly, Na_2SO_4 produces Na_2S , H_2O , and SO_2 with positive free energy, as is illustrated in Equations (1-2).



Thermodynamic calculations were done with data for pure compounds and do not predict interactions between the compounds. However, smelt #1 (rich in Na_2CO_3) increased the corrosion, in general, as the weight of smelt and test time were increased, while smelt #2 (rich in Na_2S) decreased the weight loss compared to weight loss for only 1% H_2S environment. Furthermore, smelt #3 (rich in Na_2SO_4 or poorer in Na_2S than smelt #2) increased the corrosion compared with tests in smelt #2. Results suggest the smelt components (Na_2CO_3 , Na_2SO_4 , and Na_2S) interact with H_2S thereby changing corrosion rates for carbon steel, although the change is not significant. The smelt after experiment appeared to develop a crust with the color changing from white to yellow. Although exact reactions due to gas/smelt interaction are not clear, our results here and those of previous studies [1-3] indicate that the smelt base components are not inert and interactions do occur which may change gas composition based on the reactions. Work is continuing to analyze the resultant gases by gas chromatography, which will increase our understanding of the gas/smelt reactions and explain some of the corrosion test results.

Effect of Sodium Chloride

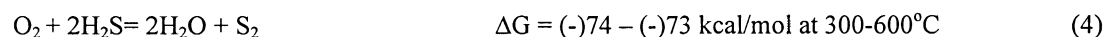
Concerns with the NaCl are that reactions of NaCl with hydrogen-containing gases may result in HCl formation under recovery boiler operating conditions. HCl at recovery boiler operating temperatures is known to be very harmful, even for 304 stainless steel [6]. Applying the same principle that H_2S reacts individually with the smelt components, thermodynamic data give positive free energy for the reaction of NaCl and H_2S that produces Na_2S , as in Equation (3).



Testing smelt #4 decreased the weight loss by 46% and 15% in 4- and 24-hour tests, respectively. Whereas, smelt #5 decreased the weight loss by 19% and 24% in the same test periods.

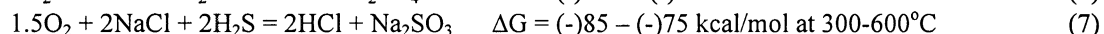
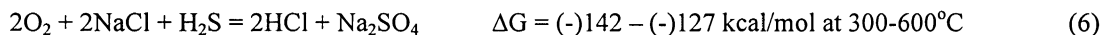
Effect of Oxygen

However, the addition of 1% oxygen to the gas mixture increased the weight loss significantly (by 83% and 170% at 4- and 24-hour tests, respectively). Oxygen reacts with H_2S to produce H_2O and S_2 with a significant negative free energy as is shown in Equation (4).



Stelling and Vegeby [1] reported that corrosion from H_2S and O_2 increases pointedly when the conditions are changed to favor the formation of sulfur. This is consistent with our observations in the present study as the presence of oxygen leads to higher production of sulfur and that caused the subsequent condensation of sulfur on the cold tube surfaces. The present study indicated a very significant increase in the corrosion rate of SA-210 specimen in 1% H_2S + 1% O_2 gas mixture. However, tests with smelt #6 reduced the weight loss of carbon steel coupon when compared with that done without smelt in 1% H_2S + 1% O_2 . Plumley, et al. [2] tested smelt constituents individually in nitrogen and air (source of O_2), and reported that tests in Na_2S showed a fourfold increase in the weight loss in air compared to the similar tests done in nitrogen. Furthermore, Fonder and Ahlers [3] reported that the addition of 5% NaCl to smelt increased the weight loss by 57%. Results from both reports were obtained by dipping the coupons into the smelt, which is different from the way the test coupons were exposed in the present work. Test coupons dipped in smelt may also undergo molten salt corrosion if some localized low-melting-point phases form at the surface of the test coupon at high temperature. Conversely, the test coupons in the present set of experiments only are only exposed to the effect of resultant gas changes. The recovered smelt at the end of testing smelt #6 was found to develop a stronger crust and close to orange color compared to yellow crust for test in only H_2S . This hard crust may stop gas permeation and gas/smelt interactions.

Tests with smelts #7 (only NaCl) were done using 50 g and the results show that the weight loss increased tremendously. The reaction of H₂S, O₂, and NaCl produces HCl with high negative free energy, as is shown in Equations (6-7).



However, gas flow in these tests with 1% H₂S + 1% O₂ and NaCl was blocked due to sulfur condensation on the cold areas of tubes. The results of tests with 10 g of smelt #7 suggest that 125 g of smelt (on basis of 4% NaCl in smelt) may be needed to produce similar effects of NaCl presence in smelt. However, this does not consider the interaction of other smelt components with initial gases. Tests with 125 g of smelt cannot be done in the present setup due to concern that the gas flow will be blocked in such a test. However, smelt with a very high NaCl content (higher than the maximum practical NaCl content) should be tested. That will allow us to see if the interaction of NaCl and other smelt components with H₂S + O₂ gas mixture results in a more corrosive gaseous mixture as is predicted by simple thermodynamic calculations.

CONCLUSIONS

1. The presence of smelt increased the weight loss of SA-210 carbon steel by 25% in the case of smelt #1 (80% Na₂CO₃, 12% Na₂SO₄, 8% Na₂S), but decreased the weight loss by 9% in the presence of smelt #2 (65% Na₂CO₃, 15% Na₂SO₄, 20% Na₂S) in 24-hour tests when compared to similar tests conducted in 1% H₂S gas mixture only. Weight loss in the presence of smelt #3 was between the weight loss results of smelt #1 and smelt #2. The smelt developed a crust with yellow color.
2. The presence of O₂ in the gas mixture (as in 1% H₂S + 1% O₂ gas environment) increased the weight loss by 170% in the 24-hour test compared to similar tests done in 1% H₂S gas.
3. The addition of NaCl to smelt by percentage (2 to 4% in smelt), which may be expected in recovery boilers, did not change the weight loss significantly when the tests were done with 1% H₂S as well as 1% H₂S + 1% O₂ gas mixture. The smelt developed a strong crust with orange color.
4. Using NaCl only (without smelt) increased the weight loss of SA-210 carbon steel in 1% H₂S + 1% O₂ gas mixture by 217% when compared to test results without salt.

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Table I. Chemical composition of SA-210 carbon steel alloy.

Element	C	Mn	Si	P	S	Fe
Weight %	0.21	0.65	0.22	0.01	0.016	Bal.

Table II. Chemical composition of smelts used in this work.

SMELT	CHEMICAL COMPOSITION
Smelt #1	80% Na ₂ CO ₃ , 12% Na ₂ SO ₄ , and 8% Na ₂ S
Smelt #2	65% Na ₂ CO ₃ , 15% Na ₂ SO ₄ , and 20% Na ₂ S
Smelt #3	65% Na ₂ CO ₃ , 27% Na ₂ SO ₄ , and 8% Na ₂ S
Smelt #4	Smelt #2 + 2% NaCl
Smelt #5	Smelt #3 + 2% NaCl
Smelt #6	Smelt #3 + 4% NaCl
Smelt #7	100% NaCl

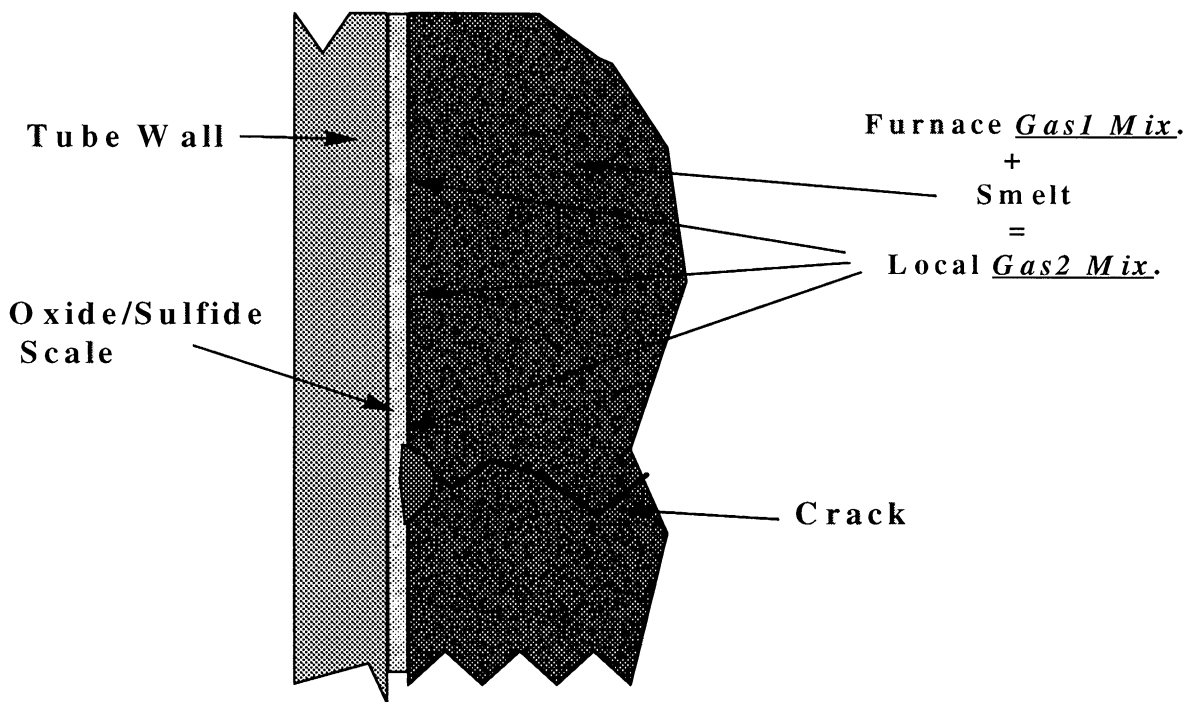


Figure 1. Schematic diagram showing access of the reactant gas mixtures from the lower furnace of the recovery boiler to the water wall tube surfaces through frozen smelt.

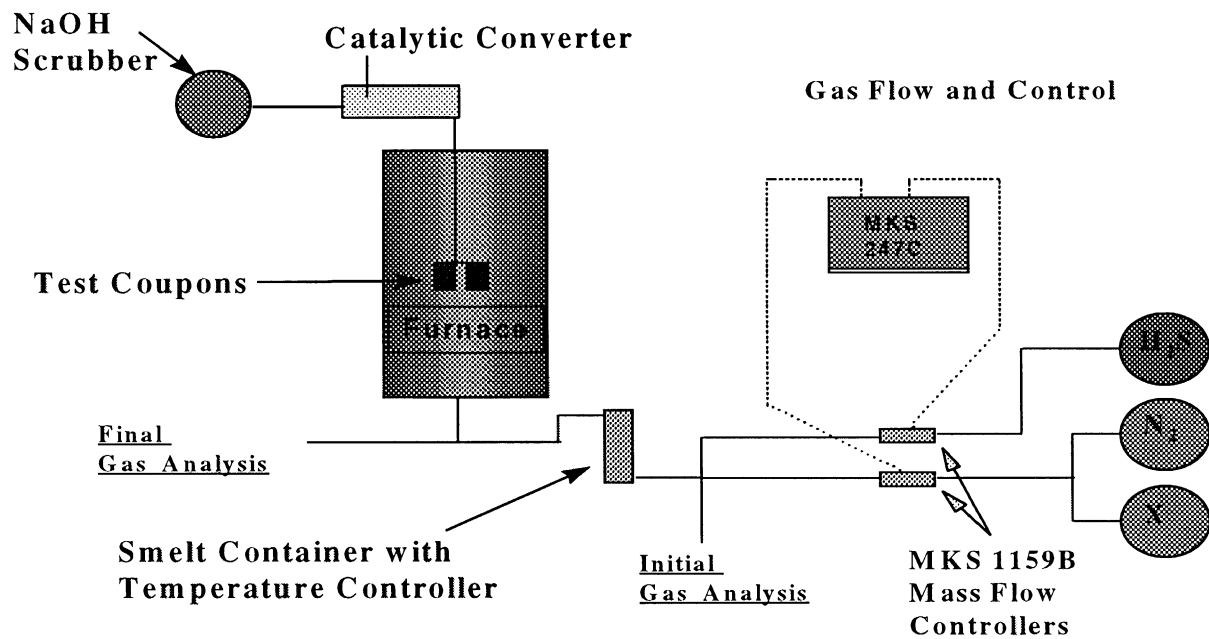


Figure 2. Schematic diagram of the experimental apparatus used in the present work.

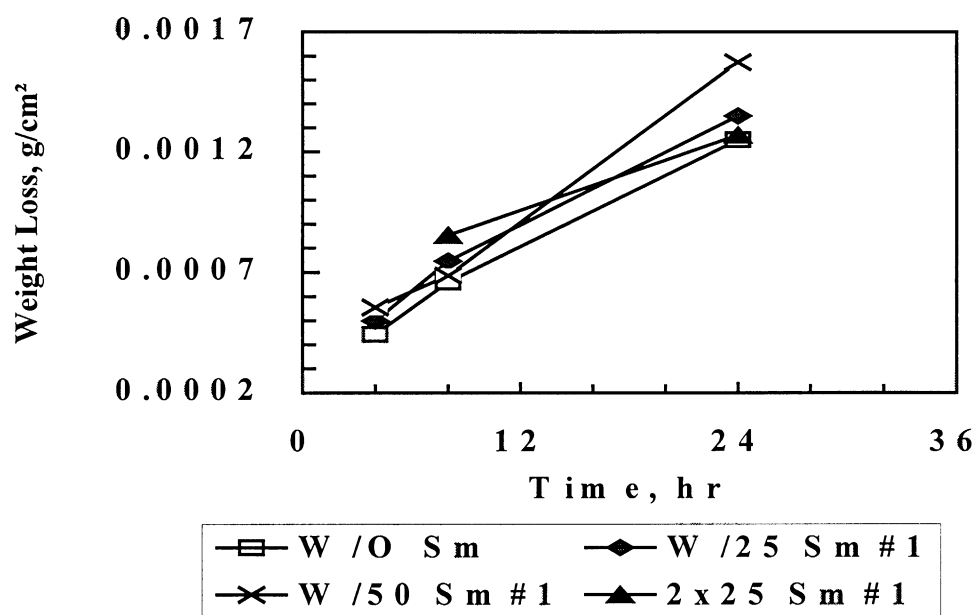


Figure 3. The weight loss of SA-210 carbon steel in 1% H₂S and smelt #1 at 400°C.

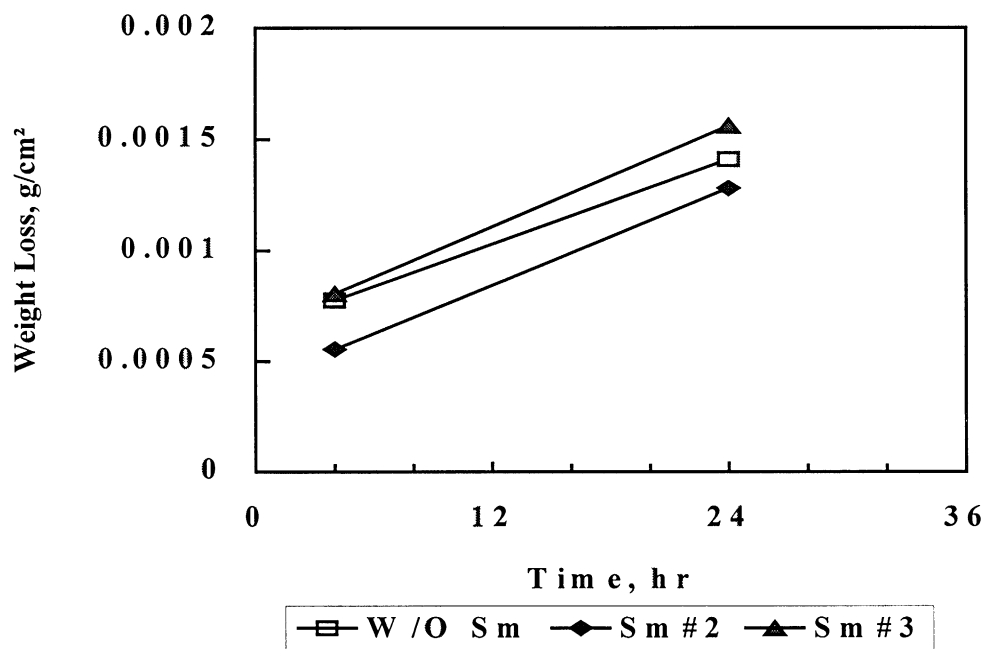


Figure 4. Weight loss of SA-210 carbon steel in 1% H₂S gas mixture at 400°C.

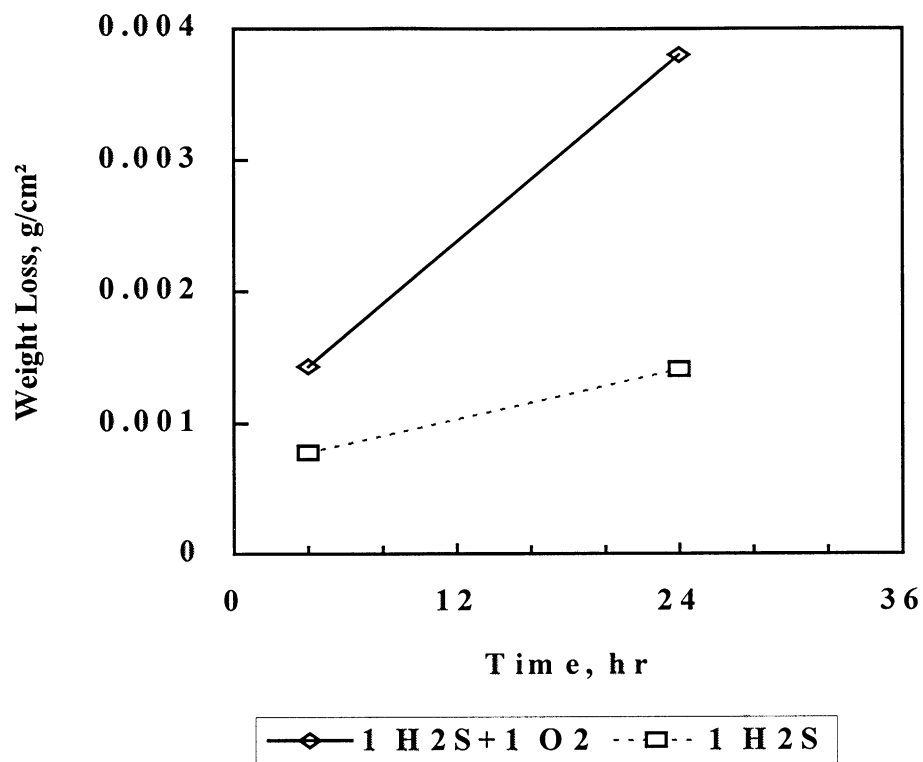


Figure 5. The effect of oxygen on the weight loss of SA-210 carbon steel in 1% H₂S + 1% O₂ at 400°C.

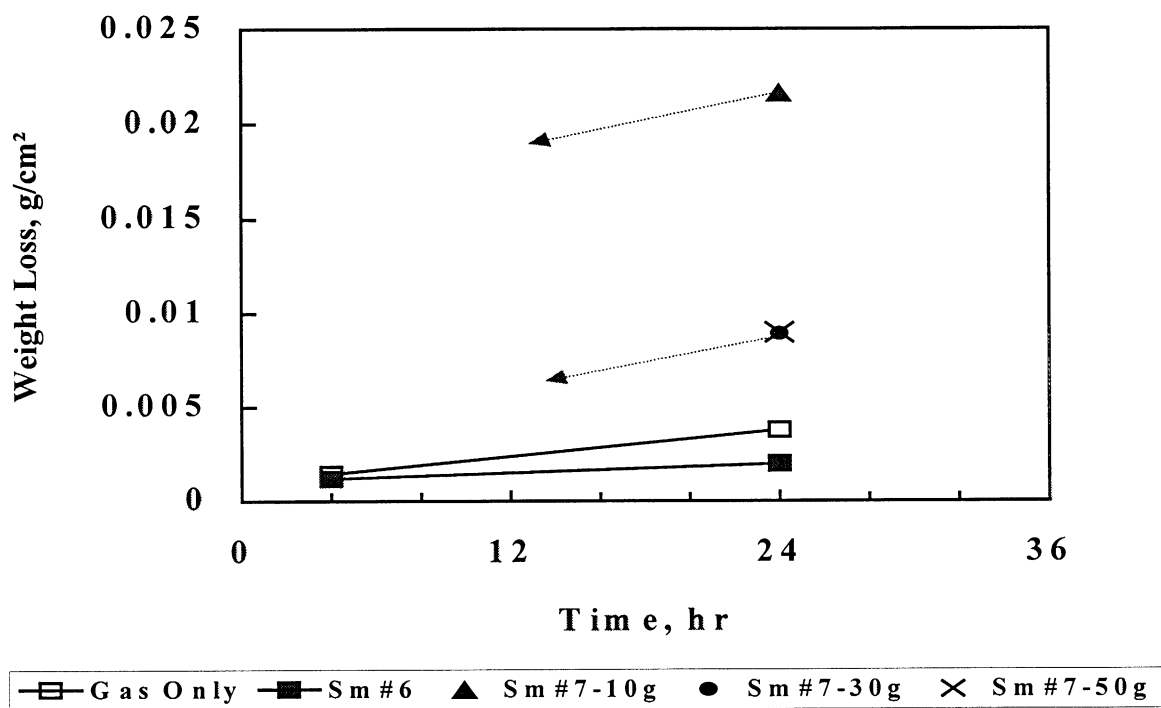


Figure 6. The effect of smelt #6 and different weights of smelt #7 on the weight loss of SA-210 carbon steel in 1% H₂S + 1% O₂ at 400°C.

