INFLUENCE OF NITRATE ON PITTING CORROSION OF TYPE 316L STAINLESS STEEL IN FGD PROCESSES

YOSHIHARU TOSHIMA, TETSUNOSUKE HASHIMOTO, KATSUYUKI NAITO, EIICHI YAMAMOTO AND YOSHO KOGAWA
Chiyoda Chemical Engineering and Construction Co., Ltd., Kawasaki 210

In flue gas desulfurization plants, which remove sulfur dioxide from the flue gas of oil and coal, chloride coming from the flue gas and makeup fresh water is accumulated in circulating absorbent. When stainless steels are employed as construction materials, pitting corrosion due to Cl− cannot be disregarded.

The Cl− concentration is usually controlled below a certain value to avoid pitting corrosion by discharging part of the absorbent (i.e., plant fluids) from the system. Inhibiting effects of NO3−, which also comes from flue gas, co-existing with Cl− in the absorbent were systematically investigated. As a result, operating instructions for actual plants are successfully established to protect stainless steel from pitting corrosion.

Introduction

In flue gas desulfurization plants where sulfur dioxide in flue gas is removed by an absorbent, chloride coming from the fuel is absorbed by the absorbent, and makeup fresh water simultaneously carries chloride into the absorbent. The chloride is accumulated in the circulating absorbent. When stainless steels are employed as construction materials, their corrosion by localized attack, called pitting corrosion, due to highly concentrated Cl− cannot be disregarded. Indeed, pitting corrosion occurred at one of the early commercial plants. To find the sources of such pitting corrosion and to avoid it, investigations were performed under conditions simulated to resemble those of actual plants.

Figures 1 and 2 show the two processes of FGD plants. Figure 1 is a process flow diagram of the dilute sulfuric acid-gypsum FGD process (hereinafter called Process A). Part of the sulfur dioxide dissolved in the absorbent is converted to sulfuric acid by the oxidizing catalyst and the injected air. Sulfuric acid is recycled in the absorption and oxidation section. The excess is sent to the crystallization section where it is neutralized by the limestone slurry to form gypsum as a byproduct.

Figure 2 is a process flow diagram of the jet bubbling FGD process (hereinafter called Process B). The flue gas is jet-bubbled into the absorbent in which sulfur dioxide is converted to gypsum by reacting with limestone and injected air.

Typical operating conditions of Processes A and B

Fig. 1 Process flow diagram for Process A

Fig. 2 Process flow diagram for Process B
are shown in Table 1. These are very corrosive conditions, and plants are normally constructed using corrosion-resistant materials. Although the operating conditions of Process A are very corrosive because of low pH, Type 316L has good resistance to general corrosion because the catalyst in the absorbent, Fe<sup>3+</sup>, acts as a passivator for Type 316L stainless steel<sup>3</sup>. In the case of Process B the absorbent contains little Fe<sup>3+</sup>, but general corrosion of Type 316L does not occur owing to a relatively high pH.

Part of the NO<sub>3</sub> in the burned product is accumulated as NO<sub>2</sub> in the absorbent. It is well-known that NO<sub>2</sub> is effective in inhibiting pitting corrosion of stainless steel<sup>1,2</sup>. While realizing the value of Uhlig and Gilman’s data, it must be recognized that these data cannot be directly applied to the actual plant. The reason is that Uhlig and Gilman’s tests were for 4- and 24-hour exposures using small specimens (6.4 x 2.5 x 0.3 cm). To determine the applicability of such inhibiting effects to an acidic environment such as those in Processes A and B, a series of corrosion tests for FGD processes have been performed since Dec. 1974. The results are discussed below.

1. Experimental

Conventional Type 316L stainless steels were used as specimens. Their chemical compositions are shown in Table 2. Immersion tests were conducted to determine the susceptibility of Type 316L to pitting corrosion. Three kinds of specimens, called Specimens X, Y and Z, were used, as shown in Table 3. Specimens Y and Z each have a weldment and their surfaces were partly ground by a hand grinder because the actual equipment made of Type 316L has areas which are locally ground when fabricated. Specimen Z was made to closely resemble actual conditions as shown in Fig. 3.

1.1 Experimental procedure for Process A

Investigations of the effect of NO<sub>3</sub> were carried out under an environment simulating Process A. 2.5 wt% H<sub>2</sub>SO<sub>4</sub> solution containing Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> at 2000 ppm as Fe<sup>3+</sup> with additions of reagent-grade NaCl and NaNO<sub>3</sub>, respectively, was used as the test solution. Hereinafter, this solution is called Solution A. The test specimens were degreased with acetone and dried before exposure to the test solution.

In the laboratory immersion test, Specimens X and Z were immersed in the test solution in the experimental apparatus shown in Figs. 4 and 5, respectively. Only the outer surface of the cylindrical Specimen Z was exposed to the test solution. The ratio of test solution volume to surface area was 14 ml/cm<sup>2</sup> for Specimen X and 8 ml/cm<sup>2</sup> for Specimen Z. The temperature was kept at 60°C using the constant-temperature water bath or the mantle heater. To simulate the operating conditions of actual plants, a loop test using Specimen Y was also conducted, using the apparatus shown in Fig. 6. The test solution volume was around 120 liters. The temperature was kept at 60°C. Also, air was injected to simulate actual plant conditions as nearly as possible. The test solution was recycled in the apparatus at a flow rate of 5000 liters/h. The ratio of test solution volume to surface area was approximately 130 ml/cm<sup>2</sup>.

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After 30 days of laboratory and loop tests, the tendency toward pitting corrosion was evaluated by measuring the weight loss of Specimen X. In the case of Specimens Y and Z, this was done by liquid penetrant examination under low-power magnification.
1. Experimental procedure for Process B

The immersion test was conducted in an environment simulating Process B. Specimen Z was immersed in the test solution in the apparatus as shown in Fig. 5, and the experimental procedure was similar to that of Process A. Deionized water with additions of reagent-grade CaCl₂ and Ca(NO₃)₂ was adjusted to pH 4.5 with dilute H₂SO₄ or NaOH. Hereinafter, this test solution is called Solution B. Air was injected into Solution B twice a week for 2 hours each time at a flow rate of 50 m³/min.

2. Results and Discussion

2.1 Corrosion tests in Solution A

To apply the experimental data to actual plants, investigations relating to the following were carried out:

a) Test duration
b) Surface condition of specimen and weldment
c) Effect of fluid flow
d) Impurities in the absorbent and air injection

1) Effect of test duration Pitting corrosion usually requires an extended initiation period, namely an incubation time, before visible pits appear. Figure 7 shows the effect of Cl⁻ and NO₃⁻ concentrations on incubation time in regard to Specimen Z. Once pitting corrosion occurred, the color of the test solution changed from yellow to green because the metal ion dissolved into the test solution. Accordingly, the time required to change color was regarded as the incubation time. When the immersion test was continued after that, pungent brown gas was released from the test solution. NO₂ gas was probably formed by the reduction of NO₃⁻ in the solution. The pits were deep, and certain areas of Specimen Z (3 mm in thickness) were perforated in a few days. Although the above incubation time is probably longer than the real period prior to initiation of pitting corrosion, these differences may be slight. Since Solution A is acidic and contains Fe³⁺ as a strong oxidizing agent, pitting corrosion is expected to proceed rapidly after nucleation of the pits.

When the Cl⁻ concentration was high, the incubation time was short (within 10 days). At each NO₃⁻ concentration, when the Cl⁻ concentration reached a certain value, the incubation time increased remarkably to 30-50 days. This tendency was observed regardless of NO₃⁻ concentration.

Based on this data, the duration of laboratory and loop tests was set at 30-50 days.

2) Laboratory test The form of corrosion of the specimen was not general corrosion, but pitting corrosion. The strong oxidizing agent, Fe³⁺, in Solution A leads to suppression of general corrosion in an acidic medium. Most of the pits were scattered in the end-grain surfaces of Specimen X. The observed pits were of the typical closed type. Most of the passive film on the metal surface remained and the metal within the pits had aggressively dissolved. Figure 8 shows the results of the immersion test using Specimen X. The allowable Cl⁻ concentration increased as the NO₃⁻ concentration increased. Allowable Cl⁻ concentration is defined as the maximum concentration at which pitting corrosion of Type 316L continues to be inhibited. The linear relation...
Fig. 8 Effect of Cl$^-$ and NO$_3^-$ concentrations on pitting corrosion of Type 316L (Specimen X)

Fig. 9 Effect of Cl$^-$ and NO$_3^-$ concentrations on pitting corrosion of Type 316L (Specimen Z)

Fig. 10 Effect of Cl$^-$ and NO$_3^-$ concentrations on pitting corrosion of Type 316L (Specimen Z) in plant solution for Process A

is obtained in a log-log plot between NO$_3^-$ concentration [ppm] and allowable Cl$^-$ concentration [ppm].

$$\log (\text{Cl}^-) = 0.77 \log (\text{NO}_3^-) + 0.615$$ (1)

Figure 9 shows the results of the immersion test using Specimen Z containing the weldment and the ground area. It was clarified that NO$_3^-$ was very effective in inhibiting pitting corrosion, as was the case for Specimen X.

Pits were mainly observed in the ground areas, and the number of pits decreased in the following order: the ground areas, the weld metal, the base metal. The shape of the pit was of the typically closed type, as in Specimen X.

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The linear relation is obtained in a log-log plot between NO$_3^-$ concentration [ppm] and allowable Cl$^-$ concentration [ppm].

$$\log (\text{Cl}^-) = 1.53 \log (\text{NO}_3^-) - 2.31$$ (2)

The allowable Cl$^-$ concentration of Specimen Z was considerably reduced compared with that of the smaller-size Specimen X because Specimen Z had a weldment and ground area.

When Specimen Z was immersed in Solution A containing approx. 3 wt% SO$_4^{2-}$ without NO$_3^-$, pitting corrosion occurred even when Solution A contained 50 ppm Cl$^-$ as shown in Fig. 9. This may indicate that the influence of SO$_4^{2-}$ on pitting corrosion is not remarkable.

The test solution was adjusted by chemically pure reagent in the laboratory. However, the absorbents used in actual plants contain a variety of impurities which may affect pitting corrosion. Absorbent was sampled from an actual plant, and NaCl and NaNO$_3$ were added to it. Figure 10 shows the results of the immersion test of Specimen Z in the plant solution. The linear relation is obtained in a log-log plot between NO$_3^-$ concentration [ppm] and allowable Cl$^-$ concentration [ppm].

$$\log (\text{Cl}^-) = 1.26 \log (\text{NO}_3^-) - 1.27$$ (3)

It was found that the allowable Cl$^-$ concentration of Specimen Z in the plant solution was similar to that in the laboratory solution.

The influence of temperature on pitting corrosion was also investigated. The allowable Cl$^-$ concentration increased remarkably at 40°C to twice the value at 60°C; on the other hand, at 80°C it decreased a little compared with 60°C.

3) Loop test Figure 11 shows the results of the immersion test of Specimen Y in the apparatus having a circulation loop. The allowable Cl$^-$ concentration in the loop test of Specimen Y was lower than that of the laboratory data of Specimen X, and higher than that of Specimen Z.

Pits were mainly observed in the ground areas, and the number of pits decreased in the following order:
the ground areas, the weld metal, the end-grain surfaces, the base metal. In laboratory immersion tests allowable Cl~ concentration of Specimen Z was lower than that of Specimen X, as shown in Figs. 8–10. The reason might be that the film on the ground surface of Specimen Z became more vulnerable than that on the end-grain surfaces of Specimen X, and the pitting corrosion resistance of the weldments on Specimen Z also decreased.

The data obtained from the loop test is presumably more realistic than the laboratory data because the loop test was carried out under conditions of flow, and the ratio of test solution volume to surface area was closer to those of actual plants.

4) Application to actual plants Based on the experimental data, a safety region determined by the Cl~ and NO3~ concentrations to prevent pitting corrosion was established in consideration of plant safety. Afterwards, some actual plants have kept their absorbents within this safety region during operation.

The plant materials exposed to the absorbents have been inspected at every shutdown, and the absorbents have been analysed periodically. Figure 11 shows some of the loop test and actual plant data on the established Cl~-NO3~ relationship. Pitting corrosion has never been observed at an actual plant since the Cl~ and NO3~ concentrations in the absorbent have been kept within the established safety region. In other words, corrosion in actual plants has been successfully prevented.

2.2 Corrosion tests in Solution B

1) Laboratory test Figure 12 shows the results of immersion test of Specimen Z in Solution B (pH 4.5). The higher the NO3~ concentration in Solution B, the higher the allowable Cl~ concentration as with Solution A. Therefore, it was verified that NO3~ also had a strong inhibiting effect on pitting corrosion in Solution B. The required ratio of NO3~ to Cl~ is less in Solution B than in Solution A. The linear relation is obtained in a log-log plot between NO3~ concentration [ppm] and the allowable Cl~ concentration [ppm].

$$\log (Cl^-) = 1.01 \log (NO_3^-) + 0.099$$ (4)

Table 4 shows the maximum pit depths at various Cl~ concentrations for Specimen Z tested in Solution B. Maximum pit depth increased with the increase in the Cl~ concentration. Table 5 shows the changes in pit depth and frequency of Specimen Z in Solution B containing 3000 ppm NO3~ and 6000 ppm Cl~. Maximum pit depth and number of pits increased with time up to 150 days, but remained almost constant after 150 days. This is believed to take place due to the fact that the growth rate of pitting corrosion in
Solution B is low compared with Solution A because pH level is higher and the concentration of the oxidizing agent Fe$^{3+}$, which strongly affects the initiation and propagation of pitting corrosion, is negligible in Solution B.

2) Pilot plant experience The pilot plant treating flue gas at an approximate rate of 3000 Nm$^3$/h contained a jet bubbling reactor made of Type 316L. After the plant was operated with the addition of Cl$^-$ and NCV in the absorbent, it was examined carefully to check whether the jet bubbling reactor suffered from corrosion or not. Figure 13 shows the plots of pilot plant data on the established Cl$^-$--NO$_3^-$ relationship. The pilot plant experience supported the laboratory data.

Therefore, it is verified that the data obtained may be applied to actual plants with high reliability. This was also confirmed in the larger-size plant (90,000 Nm$^3$/h flue gas capacity) constructed for Gulf Power Co. and operated for 10 months in Sneads, Florida, U.S.A.

Conclusion

When stainless steels are employed as construction materials for FGD plants, pitting corrosion due to Cl$^-$ in the absorbent cannot be disregarded. Accordingly, systematic investigations of Type 316L, which resisted general corrosion, have been performed in order to avoid pitting corrosion.

As a result, it was clarified that NO$_3^-$ co-existing with Cl$^-$ in the absorbent was very effective in inhibiting pitting corrosion. Based on the data obtained, a safety region determined by the Cl$^-$ and NO$_3^-$ concentrations was established. Judging from actual plant experience, it is verified that pitting corrosion is avoidable by controlling the NO$_3^-$ concentration as well as the Cl$^-$ concentration in the absorbent of FGD plants.

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Literature Cited