

CORROSION OF PIPELINE STEELS IN SLURRY OF THERMAL POWER PLANT : A CASE STUDY HIMANSHU SHEKHAR SHUKLA^{*}, NILESH HALDAR and G. UDAYABHANU

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ABSTRACT

Corrosion of slurry handling systems is a serious problem and failure of pipelines transporting slurries can result in shutting down of the whole operation causing huge financial loss to the industry. Keeping the above in view the present investigation was planned for studying the corrosion behavior of two commonly used pipeline materials, namely cast iron and mild steel, in fly ash slurries at different concentrations and pH values. The results of the corrosion rate study of mild steel and cast iron in fly ash slurries at five different concentrations from 10% to 50% w/v and in water at pH 6 for durations of 3 and 6 hours were carried out. Experiments were conducted to ascertain the corrosion rates of mild steel and cast iron in water at three different pH (pH = 6, 7 and 8). These experiments were repeated in 20% fly ash slurry adjusted to the above pH values. Scanning Electron Microscopic study of mild steel and cast iron before and after corrosion in 20% fly ash slurry adjusted to pH 6, 7 and 8 have been done. Varying the pH of the slurry had a significant effect on the corrosion rates. Maximum corrosion rate for mild steel was observed at pH 8 with the order pH 8 > pH 6 > pH 7 and for cast iron at pH 6 with the order pH 6 > pH 8 > pH 7. Scanning Electron Microscopy of corroded samples show that damage caused is more extensive in cast iron than mild steel under similar conditions. This might be due to the more heterogeneous microstructure of cast iron compared to that of mild steel.

Key words: Slurry, Mild steel, Cast iron, pH, Micrographs, Corrosion.

INTRODUCTION

Corrosion in slurries is a serious problem now days as slurries are being transported through metal pipelines over large distances. Presence of solid particles in the slurry can accelerate the process of corrosion. Pipeline corrosion accompanied by the wear caused by solids is a major problem in slurry transport systems. Failure of a single pipe can lead to the

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shut down of the entire operation as well as cause environmental damage. It is therefore extremely important to study in the laboratory the erosion-corrosion/corrosive wear of pipeline materials, before designing a slurry transport system. Duignan and Lee¹ had published an excellent review of slurry wear evaluation. It is reported that there are eight different mechanisms² for a particle to erode a substance and there are equal number of environments where such wear would take place. The problems become more complicated when particle-to-particle interaction^{3,4} and corrosion as well as the synergistic effect of corrosion and erosion⁵⁻⁸ are taken into account. Das et al.⁹ had studied the effect of slurry composition and speed on the erosive corrosive wear of aluminium alloy composites in acidic and saline media. The study reported that the wear rates increased with increasing solid content and speed, irrespective of the material used. Shipway and Wirojanupatump¹⁰ studied the role of lubrication and corrosion in abrasion of materials in aqueous environments and reported that in acid slurry the higher corrosion rate lead to an increase in the rate of material removal over that of the neutral aqueous conditions. Zhou et al.¹¹ in a study on erosion corrosion characteristics of ductile cast iron observed that erosion-corrosion wear resistance of martensitic ductile cast iron increased with the increase in pH of the slurries as well as the impact angle. The wear mechanism was reported to be dominated by the solid particle micro cutting and medium corrosion in acidic slurry and solid particle micro cutting wear in neutral and alkaline slurry. Zhenlin et al.¹² studied the corrosion abrasion of 6% chromium martensitic cast steel containing 0.35-0.95% carbon at pH values 5, 7 and 10 and they reported that the corrosion-abrasion wear resistance of 6% chromium martensitic steel with same carbon content was in the order neutral > alkaline > acidic where as the corrosion rate was in the order neutral < alkaline < acidic.

The present study deals with the results of a preliminary corrosion behavior of two commonly used pipeline materials (cast-iron and mild steel) in fly ash slurries at different pH and solid content.

EXPERIMENTAL

Cast iron and Mild steel pipe samples were procured from National Thermal Power Corporation (NTPC), Vindhyachal Super Thermal Power Project. These pipes were cut into small pieces; the sizes of the final samples of cast iron were about 3.75 cm x 1.35 cm and about 0.95 cm thickness. Mild steel samples were of 3.65 cm x 1.40 cm and thickness 0.76 cm. A small hole of 1mm diameter was drilled about 5 mm from one of the edges of the sample for enabling to fix the sample for corrosion study. The sample pieces were then made flat using a polishing machine. Using emery papers of different fineness, rough, fine and

finest, fine polishing of the samples were carried out. After fine polishing the samples were washed with acetone and dried with the help of a dryer. The samples were then stored in desiccators. The average density of the cast iron sample and mild steel was determined and it is 7.88 g/cm³. In the present study of corrosion of cast iron and mild steel in solid slurries, fly ash has been selected as the solid component. Fly ash sample for this investigation was collected from the chimneystack of Bokaro Thermal Power Plant Station of the Damodar Valley Corporation. Slurries with 10%, 20%, 30%, 40% and 50% w/v fly ash contents were prepared in distilled water. The initial pH of the slurry was noted in each case. However, to ascertain the effect of pH of the slurry on corrosion of metal samples, a few experiments

were performed with slurries adjusted to three different pH values (pH = 6, 7 and 8). In each case 200 mL distilled water was taken for preparing 10%, 20%, 30%, 40% and 50% w/v slurry and pH of the solution / slurry was adjusted using dilute solution of AR grade NaOH or HCl.

In the present investigation the gravimetric method was adopted for the determination of corrosion rate. The corrosion rate in mils per year (mpy) and millimeters per year (mmpy) were obtained using the following equations.

$$R (mpy) = \frac{534 W}{DAT}$$

and, R (mmpy) = $\frac{13.56 \text{ W}}{\text{DAT}}$

Where, T = Time of exposure, in hours.

W = Weight loss of test coupon expressed in mg.

A = Area of test coupon in sq. inches, and

R = Corrosion rate in mpy or mmpy.

Two metal specimens each were screwed to a stainless steel strip, which was fitted, to a stainless steel rod and the specimens were then immersed into the slurry and fixed to a burette stand. The slurry was placed on a magnetic stirrer and was stirred at a constant rate through out the experiment. Experiments were carried out for durations of 3 and 6 hours. After the specified time of immersion the specimens were removed, washed in running water and then immersed in a cleaning solution (conc. HCl containing 50 g SnCl₂ and 20 g SbCl₃ per liter) for a brief time to remove corrosion products. It was finally washed with

running water and dried with the help of dryer before weighing. All the experiments were carried out at a temperature of $30 \pm 1^{\circ}$ C. Results of these studies are given in Table 1 and Fig. 1. For the morphological study of mild steel and cast iron samples before and after corrosion, scanning electron microscopy (SEM Model S3400N) was adopted.

| Conc. of slurry (% w/v) – | | te (mpy) after ours | Corrosion rate (mpy) after 6 hours | | |
|------------------------------|------------|------------------------|---------------------------------------|-----------|--|
| | Mild steel | Cast iron | Mild steel | Cast iron | |
| 0 | 11.89 | 87.65 | 10.73 | 80.34 | |
| 10 | 126.79 | 112.81 | 118.20 | 92.78 | |
| 20 | 296.80 | 214.65 | 169.71 | 163.52 | |
| 30 | 210.13 | 180.06 | 116.81 | 111.85 | |
| 40 | 156.32 | 139.41 | 106.18 | 103.89 | |
| 50 | 119.88 | 107.98 | 97.46 | 86.91 | |

 Table 1: Comparison of corrosion rates of mild steel and cast iron in fly ash slurries of different concentration

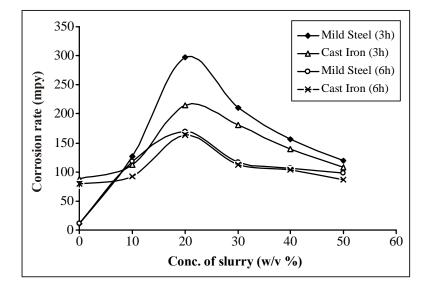


Fig. 1: Corrosion rates of mild steel and cast iron in fly ash slurries at different concentration

RESULTS AND DISCUSSION

Corrosion of mild steel in fly ash slurries at different concentrations

The results of the corrosion study of mild steel in water at pH 6 and in fly ash slurries at five different concentrations (10%, 20%, 30%, 40% and 50% w/v) for duration of 3 hours and 6 hours are presented in Table 1 and Fig. 1. It has been found that corrosion rate increases with increasing concentration of fly ash content up to 20%, but beyond that the corrosion rate progressively decreases. Addition of 10% fly ash increases the corrosion rate more than tenfold (11.89 to 126.74 mpy). This shows the increase in the aggressive wear by the medium on the addition of fly ash. Fly ash contains substantial amount of silica, which can cause abrasion of the surface. Removal of corrosion product from the surface and prevention of passive layer formation may be some of the reasons for this enhanced corrosion. This effect appears to increase by increasing the solid content up to 20%, but beyond which it has an opposite result. Higher concentrations of solid content in the slurry might have slowed down the movement of solid particles and its impingement velocity resulting the comparatively slower removal of corrosion product from the surface and formation of passive layer may get more time which lead to the decrease in corrosion rate. However these corrosion rates are still higher than that of mild steel sample in water at pH 6. It may be noted from the figure that the increasing the duration of the test has resulted in a reduction in the corrosion rate.

Corrosion of cast iron in fly ash slurries at different concentrations

The result of the corrosion rate study of cast iron in water at pH 6 and in fly ash slurries at five different concentrations (10%, 20%, 30%, 40% and 50% w/v) for durations of 3 hours and 6 hours are summarized in Table 1 and Fig. 1. Here also the trend is similar to that observed in the case of mild steel. Corrosion rate increases with increasing solid content up to 20% and then decreases with further increase in solid content. There is a 1.25 times increase in the corrosion rate by the addition of 10% fly ash slurry.

A comparison of corrosion rate reveals that even though cast iron exhibits a higher corrosion rate in distilled water at pH 6, the corrosion rate in slurries is slightly lower than that of mild steel. This may be happening due to higher hardness of cast iron compared to mild steel. However further extensive experimentation with different concentrations of slurry and duration of immersion is necessary to conclusively say anything about this. It has been found that there is significant increase in the corrosion rate of both mild steel and cast iron after the addition of fly ash to corrosive medium. The increase was observed to be more in case of mild steel (from 0.30 mmpy to 7.54 mmpy for 20% slurry) whereas in cast iron

(from 1.79 mmpy to 5.45 mmpy for 20% slurry). Increasing the duration of exposure of the metal samples to the corrosive medium resulted in a decrease in the corrosion rate.

Effect of pH on the corrosion rate of mild steel and cast iron

Experiments were conducted to ascertain the corrosion rates of mild steel and cast iron in water at three different pH values (pH = 6, 7 and 8). These experiments were performed in 20% fly ash slurry adjusted to the above pH values. Results of these experiments for mild steel and cast iron are presented in Table 2 and 3. A perusal of Table 2 indicates that the corrosion rate of mild steel first decreases on increasing the pH from 6 to 7 and then increases when it is increased to pH 8, however the increase in corrosion rate while going from pH 7 to pH 8 is much more than the change when the pH is increased from pH 6 to 7. The observation in the case of cast iron is also exactly same even though the corrosion rates are higher. The higher corrosion of cast iron may be due to their more heterogeneous structure compared to that of mild steel.

It is also interesting to note that after the immersion test the final pH of the solution increases if the initial pH is below 7 and decreases if it is equal to or greater than 7. The final pH of the slurry in all the experiments ranges from about 6.16 to 7.50.

In 20% fly ash slurry mild steel showed maximum corrosion (150.08 mpy) at pH 8 and minimum of corrosion at pH 7 (98.11 mpy). This trend is similar to that observed in the case of mild steel in distilled water adjusted to these pH values. In normal case corrosion is not expected to be significantly different at pH 6 and 8. In contrast to the behavior of mild steel, cast iron shows a different behavior in 20% fly ash slurry adjusted to different pH values. In this case maximum corrosion (237.92 mpy) was observed at pH 8 and minimum at pH 7 (212.70 mpy) and median at pH 8 (220.40 mpy). This trend is similar to that reported by Zhenlin et al.¹².

| Initial pH | Mild steel | | | Cast iron | | |
|------------|------------|-------|----------|-----------|-------|----------|
| | Final pH | ΔpH | CR (mpy) | Final pH | ΔpH | CR (mpy) |
| 6.00 | 6.16 | 0.16 | 11.89 | 6.25 | 0.25 | 87.65 |
| 7.00 | 6.72 | -0.28 | 7.99 | 6.47 | -0.53 | 69.53 |
| 8.00 | 6.73 | -1.27 | 23.83 | 6.51 | -1.49 | 172.12 |

 Table 2: Corrosion rate of mild steel and cast iron in distilled water at different pH after 3 hour immersion

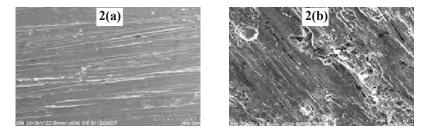
| Initial pH - | Mild steel | | | Cast iron | | |
|--------------|------------|-------|----------|-----------|-------|----------|
| | Final pH | ΔpH | CR (mpy) | Final pH | ΔpH | CR (mpy) |
| 6.00 | 7.00 | 1.00 | 116.60 | 7.03 | 1.03 | 237.92 |
| 7.00 | 7.16 | 0.16 | 98.11 | 7.25 | 0.25 | 212.71 |
| 8.00 | 7.49 | -0.49 | 150.08 | 7.50 | -0.50 | 220.40 |

 Table 3: Corrosion rate of mild steel and cast iron in 20% fly ash slurry at different pH after 3 hour immersion

A comparison of Tables 2 and 3 illustrates the effect of addition of fly ash on corrosion rate of mild steel and cast iron in water and fly ash slurry respectively. There is a significant increase in the corrosion rate of both mild steel and cast iron in presence of fly ash in the corrosive medium. However this effect is observed to be more significant in the case of mild steel. Presence of solid particles can cause constant abrasion and wear of the surface, which results in accelerated corrosion. Since the hardness of cast iron is more than that of mild steel, the increase in the corrosive medium is found to change after the immersion test for both the metal samples. This may be due to the various anodic and cathodic reactions occur on the metal surface during the corrosion process.

Scanning electron microscopic study

SEM micrographs of mild steel specimens before corrosion is given in Fig. 2(a) and that of the same sample after corrosion in 20% fly ash slurry adjusted to pH 6 in Fig. 2(b). Fig. 2(a) indicates that scratches were still left on the surface of the sample after polishing. Probably this might have had contributed to a higher corrosion rate for the specimen in the experiment and 2(b) show the sample at magnification 600, 2(b) exhibit large number of groves and pits indicating the extent of corrosion. Fig. 2(c) is that of mild steel after corrosion test in distilled water at pH 7 and 2(d) is that of the same specimen after 3 hours exposure to 20% fly ash slurry at pH 7. Fig. 2(d) indicates a more general form of corrosion at pH 7. Not many pits could be seen on these micrographs.



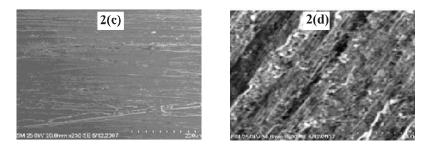


Fig. 2 (a): SEM of mild steel before exposure; (b): SEM of mild steel after exposure in 20% fly ash slurry at pH 6; (c): SEM of mild steel after exposure in distill water and (d): SEM of mild steel after exposure in 20% fly ash slurry at pH 7

Fig. 3(a) is the SEM of cast iron before corrosion and that 3(b) is that of the same specimen after exposure to 20% fly ash slurry adjusted to pH 6 for 3 hours. Fig. 3(b) indicates extensive corrosion damage with the specimens exhibiting deep pits and groves compared to mild steel. This behavior may be due to the more heterogeneous microstructure of cast iron compared to that of mild steel. Fig. 3(c) is the SEM of cast iron sample after corrosion in distilled water at pH 7 and 3(d) is that of same sample after exposure to 20% fly ash slurry adjusted to pH 7 for 3 hours. It is clearly evident from Fig. 3(b) the extensive damage the slurry had caused to the metal specimen. Here also Fig. 3(a) indicates that the sample before exposure to the corrosive medium had some small pits on its surface.

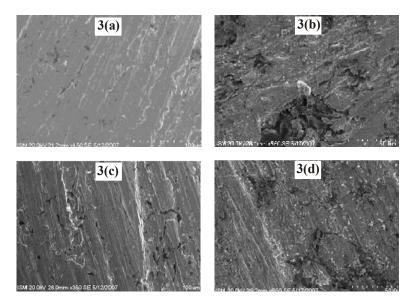


Fig. 3 (a): SEM of cast iron before exposure; (b): SEM of cast iron after exposure in 20% fly ash slurry at pH 6; (c): SEM of cast iron after exposure in distill water (d): SEM of cast iron after exposure in 20% fly ash slurry at pH 7

A comparison of the SEMs of mild and cast iron specimen clearly show that more damage occurs in cast iron than mild steel when exposed to 20% fly ash slurry. This is also corroborated by the corrosion rates of these two materials in the slurry as discussed in the earlier section.

CONCLUSION

The salient conclusions of this investigation are the following.

- (i) There is significant increase in the corrosion rate of both mild steel and cast iron after the addition of fly ash into the corrosive medium. The increase of corrosion rate is more in case of mild steel (from 11.69 mpy to 296.80 mpy for 20% slurry).
- (ii) It is found that corrosion rate increases up to 20% w/v addition of slurry for both the alloy and then the corrosion rate has shown a decreases with the addition of slurry.
- (iii) Increasing the exposure period for both the alloy samples to the corrosive medium resulted in a decrease in the corrosion rate.
- (iv) Maximum corrosion rate for mild steel was obtained at pH 8 with the order pH 8 > pH 6 > pH 7 and for cast iron at pH 6 with the order pH 6 > pH 8 > pH 7.
- (v) SEM micrographs show that the damage caused is more extensive in cast iron at similar conditions might be due to the more heterogeneous microstructure of cast iron compared to that of mild steel.
- (vi) The pH of the corrosive medium is found to change after the immersion of the metal samples. This may be due to the various anodic and cathodic reactions, which are taking place during the corrosion process.

REFERENCES

- M. R. Diugnan, and S. Y. Lee, RTP-WTP Slurry Wear Evaluation, A literature Review, WSRC-TR-2001-00156, U.S. Department of Commerce, National Technical information service, 5285 Port Royal Road, Springfield, VA22161.
- 2. C. N. A. Shook and M. C. Roco, Slurry Flow, Publ. Buttuworth Nainemann, (1991) pp. 191.
- 3. J. A. C. Humphney, Fundamentals of Fluid Motors in Erosion by Solid Particle Impact, Int. J. Heat Fluid Flow, **3**, 170-195 (1990).

- 4. Y. Xie, H. M. C. I. Clark and H. M. Hawtharec, Modeling Slurry Particle Dynamics in the Corrosion-errosion Tester, Wear, **225-229**, 405-416 (1999).
- 5. F. Umemura, S. Matukura, and T. Kawamoto, Electrochemical Study of Erosion Corrosion in Carbon Stainless Steels, Corrosion Engg., **36**, 569-578 (1987).
- 6. Y. Zheug, Z. Yao, Weix and W. Ke, The Synergistic Effect Between Erosion and Corrosion in Acid Slurry Medium, Wear, **186-187**, 555-561 (1995).
- 7. F. Aiming, L. Jimming and J. Ziyun, An Investigation of the Corrosive Wear of Stainless Steel in Aqueous Slurries, Wear, **193**, 73-77 (1996).
- Y. P. Purandare, M. M. Stack and P. En Novselpan, Velocity Effect on Erosion-Corrosion of CrN/NbN Soperlattice, PVD Coatings, Surface & Coatings Technol., 201, 361-370 (2006).
- 9. S. Das, Y. L. Saraswathi, and D. P. Mondal, Erosive-corrosive Wear of Aluminium Alloy Compsites : Influence of Slurry Composition and Speed, Wear, **261**, 180-190 (2006).
- P. H. Shipway and S. Wirojanupatump, The Role of Lubrication and Corrosion in Abrasion of Materials in Aqueous Environments, Tribology International, 35, 661-662 (2002).
- 11. Y, Zhou, Z Lu and M. Zhan, An Investigation of the Erosion-corrosion Characteristics of Ductile Cast Iron, Materials & Design, **28(1)**, 260-265 (2007).
- L. Zhenlin, R. Qichang, and J. Zhihao, An Investigation of the Corrosion-abrasion Wear Behavior of 6% Chromium Martenstic Cast Steel, J. Mat. Proc. Technol., 95(1-3), 180-184 (1999).

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