

# Water Corrosion Resistance of Metal Powders for Carbon-Containing Castables

**The use of metal powders as antioxidants for high-carbon-containing castables is feasible by selection of a suitable binder.**

Vitor G. Domiciano, Jarem R. Garcia and Victor C. Pandolfelli

A current significant trend in refractory technology is associated with the development of high-carbon-containing refractory castables (HCCCs).<sup>1,2</sup> The use of surfactants is an economic and efficient alternative to incorporate great amounts of carbon within castables. However, technical difficulties, such as poor corrosion resistance of metallic powders (aluminum, silicon and magnesium) commonly used as antioxidants, continue to hinder the production and application of these materials.<sup>1-5</sup> When they are in contact with the casting water, the metal particles hydrate (corrosion phenomena), which generates a large amount of hydrogen-gas and the loss of their antioxidant properties.

During recent years, several attempts have been made to inhibit the metal-powder-water reaction. Protective coatings obtained with metal alkoxydes have been proposed as a reasonable solution.<sup>3-5</sup> Nevertheless, no reliable references have been found to support the efficiency of these coatings in preventing metal corrosion when coated-metallic powders are added to carbon-containing castables. Moreover, some studies have pointed out that the castable high-alkaline condition promoted by cement hydration is the main reason for the corrosion of metal powders.<sup>3-5</sup> The present work outlines the latest approaches in incorporating metallic particles (aluminum and silicon powders) as antioxidants in HCCCs.

## **Metal-Powder Source, Coating Precursor, Castable Composition**

Aluminum powder (101, Alcoa, USA) and silicon powder (Silgrain, Elkem Refractories, Kristiansand, Norway) were used as antioxidants in an HCCC based on an ultra-low-cement-content  $\text{Al}_2\text{O}_3$ -SiC-SiO<sub>2</sub>-C composition (Table 1). The particle-size distribution was adjusted to a theoretical curve based on the Andreasen packing model ( $q = 0.21$ ). Sodium polymetacrylate (Darvan-7S, R.T. Vanderbilt Co., Norwalk, Conn.) and a nonionic surfactant were used as a dispersant to the castable and wetting agent for the carbon source, respectively. As-received aluminum or silicon powder was added (0.3 wt%) to the dry composition and 6.5 wt% of distilled water was used to provide cement hydration and flowability.

Three other binders were tested as alternatives to cement in the HCCC: hydratable alumina (HA; Alphabond 300, Almatix, Leetsdale, Pa.); colloidal alumina (CA; Wesol A, solids concentration of 20.0 wt%, pH (at 25°C) of 4.0, Wesbond Corp., Wilmington, Del.); and colloidal silica (CS; Nalco 00BLZ021, solids concentration of 40.0 wt%, pH (at 25°C) of 10.1, Nalco Co., USA). In these systems, the amount of HA, CA and CS added were 3.0, 8.1 and 13.0 wt%, respectively.

Two metallic alkoxydes were tested as precursors to obtain a silicon-based coating on an aluminum-powder surface: a silane (tetraethoxysilane, TEOS; Merck, Darmstadt, Germany) and an organo-silane (Z-6341, n-octiltrietoxysilane, Dow Corning Corp., Midland, Mich.). A reactive polymer (hydrogen-methyl siloxane,

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Dow Corning) also was used to coat the aluminum particles. The as-received aluminum powder was submitted to various surface treatments using the sol-gel method. The details regarding the experimental procedure conducted to coat the metal particles has been described in the literature.<sup>3</sup>

The corrosion resistance of the aluminum and silicon powders was evaluated through experiments conducted in water and in refractory castables. The hydration tests consisted of measuring the hydrogen-gas pressure developed inside a hermetic closed vessel in which metal-powder-containing castable or metal-powder aqueous suspension was placed. The sealed vessel was kept inside a water bath at a constant temperature. An electronic transducer monitored the pressure increase inside the vessel and the pressure value was recorded every 10 s during the experiment time.<sup>3</sup>

The amounts of water and metal powder used in these tests were proportional to those added to the castable. To set references, gas evolution tests were first performed with water- or metal-powder-free castable. The water corrosion resistance of the as-received metal powders then was evaluated through hydration tests conducted in water at various temperatures (30, 50 and 70°C) and in castables at 50°C. Second, the efficiency of various silicon-based coatings on inhibiting aluminum-powder corrosion was evaluated using hydration tests in water and in castable at 50°C. Third, the influence of the castable pH on the corrosion resistance of the metal powders was investigated using tests conducted in castables prepared with various binders.

### Metal Powder Hydration Resistance

The hydration tests conducted in water at various temperatures revealed a fairly distinct behavior between the metal powders. Aluminum showed poor corrosion resistance, and temperature increase was responsible for accelerating and intensifying the aluminum-water reaction. However, no evidence of silicon corrosion was detected, even in experiments conducted in water at 70°C (Fig. 1). These results showed that the silicon powder displayed a superior corrosion resistance in water (pH ~7) when compared with aluminum powder.

This superior chemical stability has been predicted using the Pourbaix diagram.<sup>6</sup> The diagram indicates that, under a wide pH range (0–10), silicon becomes protected by a thin silica layer (passivation state) formed on the metal surface as a result of a slight metal-water reaction. Also according to the diagram, silicon is attacked when exposed to aggressive alkaline aqueous solutions (pH >10), because the silica layer is dissolved, which leaves the metal surface unprotected. In the case of aluminum, the Pourbaix diagram foresees the corrosion of metal in acidic and basic aqueous solutions.<sup>6</sup> The passivation of aluminum is achieved through the development of an aluminum hydroxide protective film, stable in a narrow pH range (~4–6 when protected by a boehmite film, or 4–8 when protected by a hydrargillite layer).<sup>6</sup>

According to Pourbaix<sup>6</sup> and Hart,<sup>7</sup> the aluminum passivation process initially consists of the generation and thickening of an amorphous aluminum hydroxide protective film. For higher temperatures or longer times of water exposure (or both), this unstable coating crystallizes to give a boehmite film that then can be converted to bayerite. This promotes an increase in the chemical stability of the passivation layer and on the metal corrosion protection.<sup>6,7</sup>

Further tests performed with aluminum powder in refractory castables revealed an intense hydrogen-gas

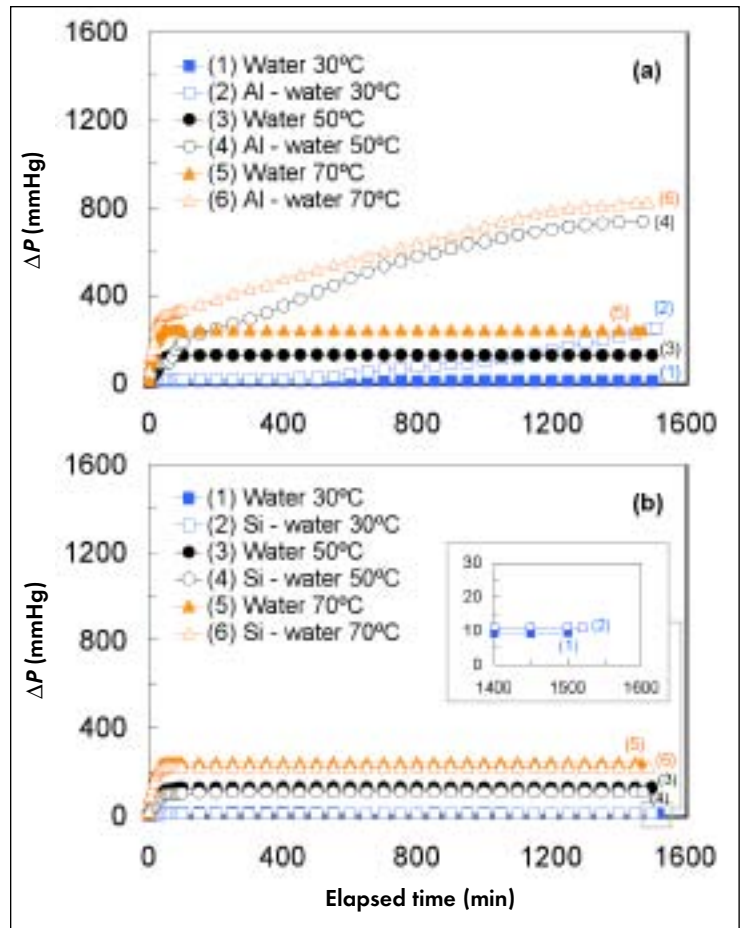


Fig. 1 Corrosion resistance of as-received (a) aluminum and (b) silicon powders in water at various temperatures.

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release as an outcome of the aluminum–water reaction (Fig. 2). In the case of silicon powder, no evidence of metal corrosion was detected, even after 24 h of testing (1440 min).

The poor corrosion resistance of aluminum powder in water and in refractory castables has shown that this metal demands better corrosion protection for its application as an antioxidant. The high corrosion resistance verified with silicon powder suggests that a silica coating can offer a superior corrosion protection to aluminum.

To investigate this hypothesis, aluminum powder was submitted to various surface treatments, which led to the formation of a silicon-based coating.<sup>3</sup> The hydration tests revealed that the silicon-based coatings (TEOS, Z-6341 and RP) performed well in inhibiting aluminum corrosion in tests conducted in water (Fig. 3(a)). However, none of the coatings were able to avoid the aluminum–water reaction when the coated powders were added to the castable (Fig. 3(b)).

The reasons for the inefficiency of the silicon-based coatings in the castables were related to the high alkaline conditions ( $12 < \text{pH} < 12.5$ ) promoted by the cement hydration.<sup>3</sup> Differences were observed in the performance of the silica protective layer formed on a silicon-powder surface through metal passivation and that obtained on the aluminum-powder surface through the coating treatments (TEOS, Z6341 and RP) in the castables (Figs. 1(b) and 3(b)). The differences might have been associated with the amorphous nature of the silicon-based coating, which could not afford the chemical stability required to withstand the castable aggressive alkaline conditions. Nevertheless, thermal treatment at 350°C on aluminum powder coated with alkoxydes and reactive polymer showed no signs of improvement when they were added to the refractory castable.

The Pourbaix diagrams emphasize the effect that the acidic–basic conditions present on the stability of the metals when exposed to water. In addition, some studies have pointed out that the alkaline conditions promoted by cement binder mainly are responsible for the metal-powder corrosion in HCCCs.<sup>3,5</sup>

To investigate the influence of castable pH on corrosion resistance of metal-powder hydration, tests were performed with castables prepared with various binders (Table 2). Hydration tests performed with aluminum-containing castables using CAC or HA as binders revealed an intense hydrogen-gas release (Fig. 4(a)).

When the pH conditions attained by these castables and the solubility of the aluminum hydroxide surface layer in alkaline environments ( $\text{pH} > 9$ ) are considered, an extensive aluminum–water reaction should be expected in these systems. Despite these two predictable results, the other experiments reveal three interesting situations.

- Binder-free castable (Fig. 4(a), curve 2): Although the alkaline conditions attained by the castable ( $\text{pH} 8.8$ ) should favor aluminum-particle corrosion, only a small gas-pressure increase is detected during the hydration test. This result could indicate, at first consideration, that the metal particles have been passivat-

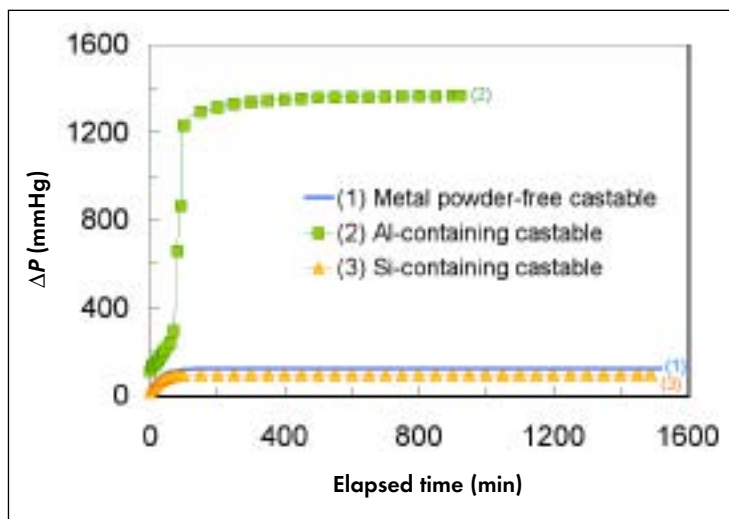


Fig. 2 Corrosion resistance of aluminum and silicon powders in refractory castables at 50°C.

Table 1 HCCC Composition

Raw material	Composition (wt%)
<b>Aggregate</b>	
White-fused alumina (EK8R, mesh 5/16–200) <sup>†</sup>	53.5
SiC (EC6R, mesh 6–200) <sup>†</sup>	17.5
<b>Matrix</b>	
Calcined alumina (A-3000FL) <sup>‡</sup>	11.0
Cement (CA-270) <sup>‡</sup>	3.0
Fumed silica (971-D) <sup>§</sup>	5.0
Coke (Unicarbo 50) <sup>¶</sup>	10.0

<sup>†</sup>Alcoa (Brazil). <sup>‡</sup>Almatis (United States). <sup>§</sup>Elkem Refractories (Norway). <sup>¶</sup>Unimetal (Brazil).

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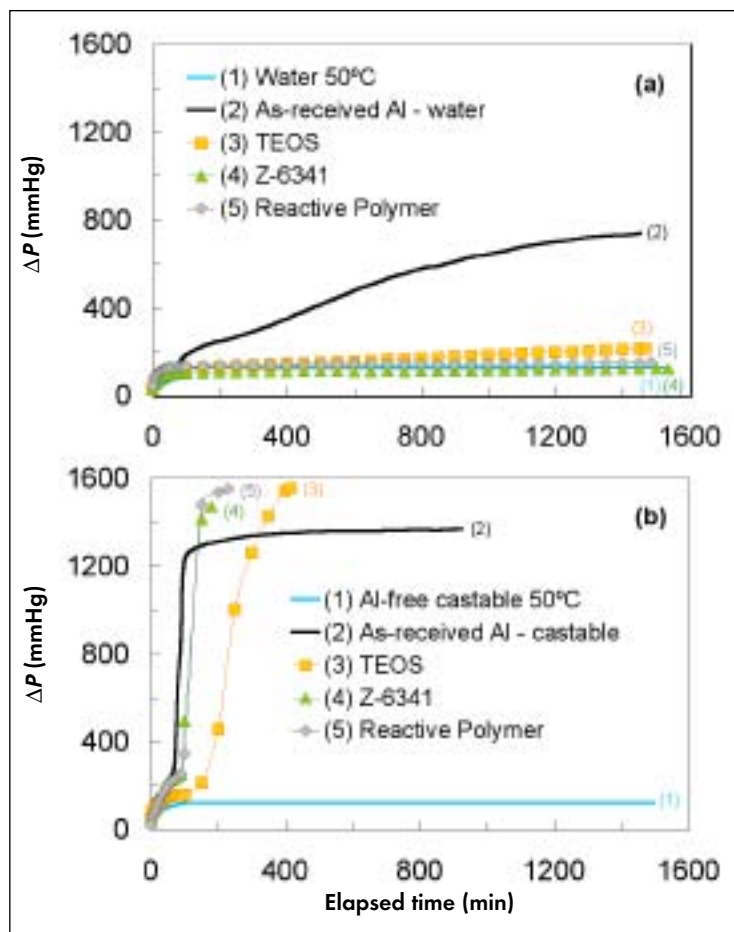


Fig. 3 Corrosion resistance of coated aluminum powder at 50°C in (a) water and (b) refractory castables.

the passivation of silicon through the generation of a silica protective layer. Unexpected behavior was observed in the tests performed with castables prepared with CAC and CS (Fig. 4(b), curves 3 and 6). According to the Pourbaix diagrams, a significant hydrogen-gas release should have been expected by the silicon corrosion at high alkaline conditions of cement-containing castables. Nevertheless, no increase on pressure levels was detected.

The same mismatch was observed for the castable prepared with CS. Although the castable developed similar pH values to those achieved by the castable prepared with HA, a small pressure increase was detected at the end of the test, which indicated a slight silicon–water reaction. This set of results revealed some limitations of the Pourbaix diagrams when predicting the passivation or corrosion of metal particles within the castables. In fact, the experiments performed by Pourbaix expressed interactions between the metals and the aqueous medium in particular circumstances.

Hence, the diagrams are valid only to represent the corrosion of the metals and the passivation phenomena within environments free of substances with which aluminum or silicon can form soluble complexes or insoluble salts.<sup>6</sup> Therefore, an unexpected passivation mechanism might be taking place in metal powders in the aluminum-containing castables prepared with CS (Fig. 4(a), curve 6) and in the silicon-containing castables prepared with CAC, HA or CA (Fig. 4(b), curves 3, 4 and 5, respectively). To explain this anomalous behavior, it is important to understand how the presence of aluminum can influence the corrosion of silicon and vice-versa. The literature points out that the presence of small amounts of aluminum decreases the rate of silica dissolution and the solubility of silica.

In the same way, the addition of silica to an alumina suspension suppresses the solubility of alumina.<sup>8</sup> Such interaction is indicative that the mechanism of metal passivation involves the formation of an insoluble aluminosilicate layer on the metal-powder surface. According to the literature, the formation of aluminosilicates requires the presence of aluminum and silicon ions and pH values >4.<sup>8,9</sup> Moreover, the min-

ed. Nevertheless, this seems not to be the most feasible explanation for such behavior. As shown later, further results confirm aluminum corrosion within the binder-free castable.

- Castable prepared with CA (Fig. 4(a), curve 5): Although the aluminum passivation should be expected within the mild acid pH values (5.7) attained by this castable,<sup>6</sup> a small but considerable increase on the pressure level is detected in the hydration test. The aluminum passivation predicted by Pourbaix in the pH ranges of 4–6 or 4–8 considers the presence of a boehmite or bayerite protective layer, respectively. However, the aluminum hydroxide layer initially formed as an outcome of the aluminum–water reaction is amorphous and at this pH condition is susceptible to dissolution. This leads to metal corrosion up to the moment that the passivation is achieved through the crystallization of the amorphous film.

- Castables prepared with CS (Fig. 4(a), curve 6): Although the castables developed similar pH values compared with those prepared with HA, no evidence of aluminum–water reaction is observed after 24 h of testing.

The tests performed with silicon powder revealed that, in the absence of binder or in the presence of HA or CA, no evidence of silicon–water reaction was detected (Fig. 4(b), curves 4 and 5). As predicted by Pourbaix, in all these tests, the castable pH conditions favored

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eral equilibrium and solution pH are responsible for regulating the concentration and type of dissolved species that determine the type of aluminosilicate formed. Based on this information, the favorable conditions for aluminosilicate formation are attained by aluminum-containing castables prepared with CS and by silicon-containing castables prepared with CAC, HA or CA where the atypical metal passivation phenomena are observed.

Although the protection mechanism discussed above seemed to be a reasonable explanation for metal-particle passivation, no support was found to enlighten the corrosion inhibition of silicon powder within the cement-containing castables. The solubility of the aluminosilicates was considerably low in the pH range 0–10,<sup>8,9</sup> but increased rapidly for higher pH values.<sup>9</sup> Thus, regarding the high pH values attained by the castables prepared with CAC ( $12 \leq \text{pH} \leq 12.5$ ), the aluminosilicate coating could not stand the aggressive alkaline conditions and the metal powder should have been corroded.

The corrosion resistance of the proposed aluminosilicate coating was evaluated and whether the corrosion inhibition could be extended to a larger antioxidant content was investigated. Hydration tests were performed in castables where 5.0 wt% of metal powder was added and the pH values were adjusted to high alkaline conditions (pH 12–12.5, using a sodium hydroxide aqueous solution). The experiments revealed that, even when a greater amount of silicon powder was added to the castables prepared with HA or CA, no evidence of metal–water reaction was detected (Fig. 5(b), curves 4 and 6). Nevertheless, when the castable pH was increased to the values attained by the cement-containing castable (12–12.5), the corrosion of silicon was evident in both systems.

On the other hand, the test conducted with cement-containing castables showed again no increase in the gas-pressure level (Fig. 5(b), curve 3), which indicated a superior corrosion resistance of the aluminosilicate coating developed in this particular system. The differences observed in these castables might have been related to the  $\text{Ca}^{2+}$  ions present during the calcium aluminate cement dissolution.

These ions can actuate as an interstitial cation within the aluminosilicate structure, providing a high chemical stability to the calcium aluminosilicate coating.<sup>8</sup> Consequently, the silicon particles present a strong corrosion resistance, even when exposed to the aggressive alkaline conditions verified in the cement-containing castable. The protection mechanism based on the aluminosilicate coating is supported by the result obtained with the castable prepared with CS. Within this system, the augment in the silicon-powder content has evidenced the metal corrosion, and the increase in the castable pH is responsible for intensifying the metal–water reaction, because the silica passivation layer does not resist to the high-alkaline environments.<sup>6</sup>

The castable hydration test performed with 5.0 wt% of aluminum powder using CS as a binder also revealed no evidence of metal corrosion (Fig. 5(a), curve 3). Nevertheless, when the castable pH was adjusted to the critical conditions for the aluminosilicate coating, a significant increase in the pressure level was observed. Concerning the test conducted with a binder-free castable, the addition of a larger aluminum-powder content made the corrosion of metal particles evident.

The results discussed above strongly support the protection mechanism based on the aluminosilicate coating, which has shown to enable the use of metallic powders as antioxidants in HCCCs. The progress achieved in this study may contribute to the continuous development of high-performance refractory materials. ■

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### About the Authors

Vitor G. Domiciano is a staff member with Magnesita Research Center, Contagem, Brazil. Jarem R. Garcia and Victor C. Pandolfelli are faculty members in the Dept. of Materials Engineering, Federal University of São Carlos, São Carlos, Brazil.

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**Table 2 pH Values of Castables<sup>†</sup>**

Castable binder	pH measurement <sup>‡</sup>		
	Metal-powder-free castable	Aluminum-containing castable	Silicon-containing castable
Binder free	8.8	8.8	6.7
CA	5.7	5.7	5.7
CS	9.4	9.4	9.5
HA	9.2	9.3	9.2
CAC	12.4	12.5	12.5

<sup>†</sup>Prepared with and without metal powder using various binders. <sup>‡</sup>pH measurements were performed after the wet-mixing step. The values represent the pH attained by the castable after its stabilization.

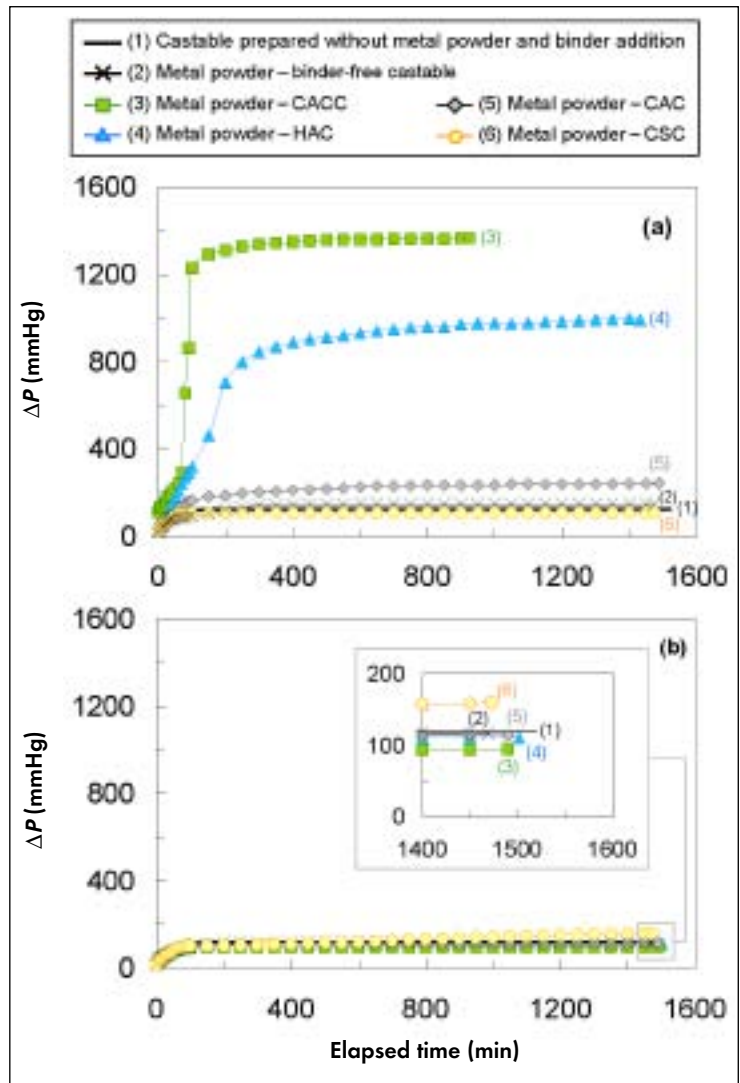


Fig. 4 Corrosion resistance of (a) aluminum and (b) silicon in refractory castables at 50°C using various binders.

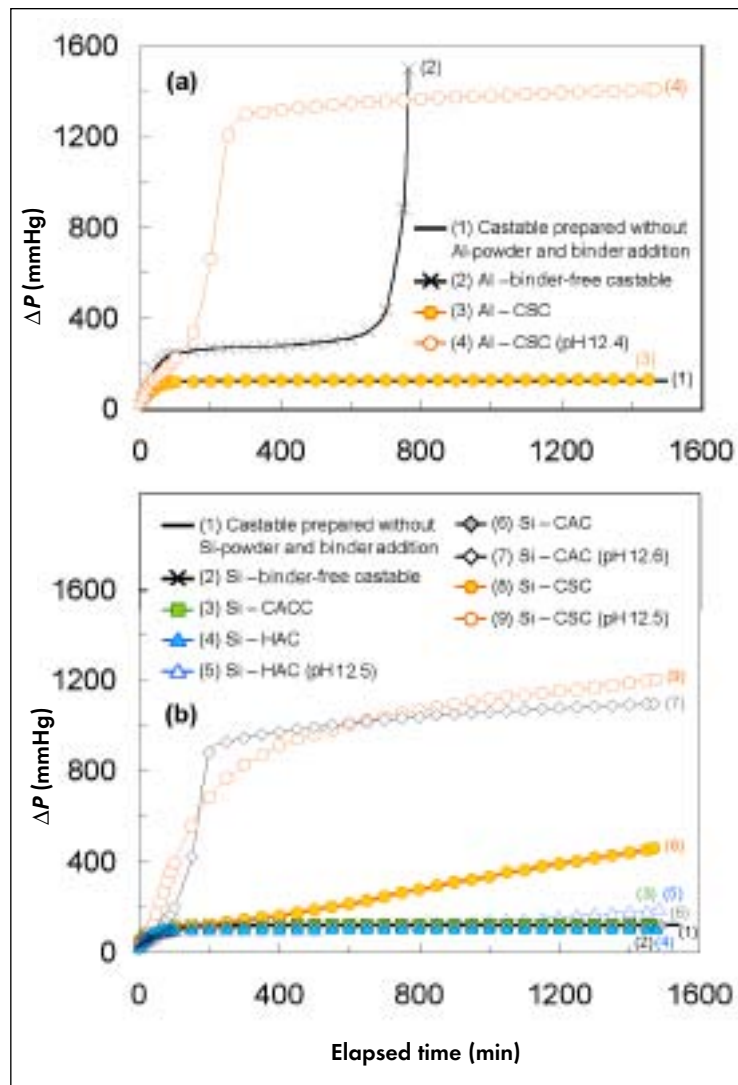


Fig. 5 Hydration tests performed with refractory castables containing 5.0 wt% of (a) aluminum and (b) silicon powders using various binders at 50°C with or without pH adjustment to alkaline conditions.