

Cast iron deterioration with time in various aqueous salt solutions

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MS received 4 June 2001; revised 21 December 2001

Abstract. The changes with time in the corrosion rate and corrosion current density on a cast iron electrode in various aqueous salt solutions have been carried out using total immersion test and potentiostatic polarization curves. The concentration of salts taken is expected to be present in potable water. The relative behaviour of these salts towards corrosion has also been studied, which is found to be different from previous studies. The total immersion test parameters viz. weight loss, corrosion rate as well as potentiostatic parameters, open circuit potential, I_{corr} , Tafel slopes, corrosion rate, have been calculated by standard methods. Besides these the relative increase in corrosion rate with time as well as the percentage to which corrosion rate should be decreased so as to provide protection towards corrosion have also been calculated. It was found that KCl and NaCl are major contributors than MnSO_4 , $\text{Pb}(\text{NO}_3)_2$, KI and KBr. The relative increase in corrosion is high in KBr, KI, NaNO_3 , CaCl_2 , and less in $\text{Pb}(\text{NO}_3)_2$, NaHCO_3 and CaCO_3 test solutions. For the reliability of results the data has been statistically analysed.

Keywords. Corrosion; cast iron; water; salts.

1. Introduction

Cast iron is widely used for water carrying purposes besides mild steel and other metals. The extent and cost of damage caused by leakage in domestic water pipes has been rising during recent years. The use of cast iron in potable water supplies in buildings is now essentially limited to the incoming main water supplies (Gedge 1993). Within buildings themselves cast iron is now generally used only for pump and valve bodies. The corrosion resistance of cast iron is however relatively better. Various studies have been carried out for determination of corrosive behaviour of cast iron in acid, its salt aqueous solutions at high concentration of salts as well as in water supply systems (Siiry 1978; Andrzejczek 1979; Weber 1979). Corrosive behaviour of metals in aqueous solutions is mainly determined by dissolved salts and oxygen (Dubey *et al* 1997). In order to minimize corrosion problem in water supply system it is important to identify the mechanism of corrosion rate of ions with cast iron, the extent to which they contribute to corrosion in potable water as well as their threshold limiting values to which the corrosion rate should be minimized in order to provide excellent corrosion resistance (Gour *et al* 1994).

2. Experimental

The $2 \times 2 \text{ cm}^2$ analysed cast iron specimens of thickness 0.5 cm were used. The specimens were cast in the die by appropriate casting procedure (Rao 1980; Kumar *et al*

1991). The chemical composition used was C–3.26%, S–0.10%, Si–2.25%, Mn–0.59%, P–0.06% besides iron, as analysed by standard method (Vogel 1964; Jain 1986). After casting, the surfaces were smoothed and a hole was drilled near the upper edge. The specimens were cleaned by buffing, degreased in benzene, washed using 50% acetone, dried, marked and weighed to a constant weight before exposing to the corrosive medium. These were suspended by a glass hook in a beaker filled with test solution, for different duration of immersions: 24, 72, 120, 192, 240 and 360 h. After definite period of exposure, specimens were removed and cleaned as per recommended procedure (Mercer *et al* 1977; Thompson 1984) in a solution of hydrochloric acid, 50 gpl stannous chloride and 20 gpl antimony chloride, dried and weighed. The authenticity of data was ascertained by reported measurements.

Experimental set up for polarization measurements consisted of potentiostat/galvanostat, model CL-95 of Elico with a sweep generator. Saturated calomel electrode was used as reference electrode. The variation of the cast iron electrode potential under open circuit conditions in the tested solution were also determined after definite period of time and subsequently anodic and cathodic potentiostatic polarization curves were drawn. All electrochemical studies were made at $28 \pm 1^\circ\text{C}$ and in each experiment 500 mL of test solution was employed (Wahab El abd and Din El Shams 1978).

Results of polarization and weight loss measurement for corrosive medium have been carried out for NaCl–600 ppm, KCl–600 ppm, Na_2SO_4 –400 ppm, CaCO_3 –400 ppm, CaCl_2 –120 ppm, MgSO_4 150 ppm, NaNO_3 –

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65 ppm, MnSO_4 –5 ppm, $\text{Pb}(\text{NO}_3)_2$ –3 ppm, KBr –5 ppm and KI –5 ppm. These will be referred to in the text as A, B, C, D, E, F, G, H, I, J, K, L. In order to determine the average contribution of each salt to the corrosion rate, a test solution containing all above salts was prepared for the study. Redistilled water was used in the preparation of all test solutions. All chemicals used were of analytical grade.

3. Results and discussion

The corrosion rate of cast iron in the test solutions was calculated from decrease in weight observed in coupons in weight loss tests using following formula

$$\text{Corr. rate (mpy)} = \frac{534 \times w}{D \times A \times T},$$

where w is weight loss (mg), D the density (g/cm^3), A the exposed area of specimen (inch^2), T the time of exposure (h).

For potentiostatic measurements potentiostatic parameters I_{corr} , E_{corr} were obtained from the slopes of linear polarization curves and corrosion rate was calculated using the following expression

$$\text{Corr. rate (mpy)} = \frac{0.129 \times I_{\text{corr}} \times EW}{D \times A},$$

where I_{corr} is corrosion current (A), EW the equivalent weight of metal (g), A the exposed area of specimens (cm^2), D the density of metal (g/cm^3) (Vashi and Champagneri 1997; Mehra and Soni 2001).

The corrosion rate was converted from mpy to mmpy using following relation

$$1 \text{ mpy} = 0.0254 \text{ mmpy}.$$

Table 1 gives the composition of various test solutions taken for the study. Table 2 shows the results of weight loss obtained by NACE standard TM-01-69 method for

Table 1. Composition of various test solutions and composite water.

Component	Concentration (ppm)	Ion concentration (ppm)												
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Pb^{2+}	Mn^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	NO_3^-	Br^-	I^-
NaCl	600	236.0	–	–	–	–	–	364.0	–	–	–	–	–	–
KCl	600	–	314.7	–	–	–	–	285.3	–	–	–	–	–	–
Na_2SO_4	400	129.5	–	–	–	–	–	–	270.5	–	–	–	–	–
CaCO_3	400	–	–	160.2	–	–	–	–	–	–	239.8	–	–	–
CaCl_2	120	–	–	43.3	–	–	–	76.7	–	–	–	–	–	–
MgSO_4	150	–	–	–	30.3	–	–	–	119.7	–	–	–	–	–
NaHCO_3	400	109.5	–	–	–	–	–	–	–	290.5	–	–	–	–
NaNO_3	65	17.6	–	–	–	–	–	–	–	–	–	47.4	–	–
MnSO_4	5	–	–	–	–	–	1.8	–	3.2	–	–	–	–	–
$\text{Pb}(\text{NO}_3)_2$	3	–	–	–	–	1.9	–	–	–	–	–	1.1	–	–
KBr	5	–	1.6	–	–	–	–	–	–	–	–	–	3.4	–
KI	5	–	1.2	–	–	–	–	–	–	–	–	–	–	3.8
Composite water	Total	492.6	317.5	203.5	30.3	1.9	1.8	726.0	393.4	290.5	239.8	48.5	3.4	3.8

Table 2. Effect of time of exposure on weight loss (mg/dm^2) in different test solutions at $28 \pm 1^\circ\text{C}$ for cast iron.

Solution	Weight loss ($\text{mg/dm}^2 \pm \text{S.D.}$)					
	24 h	72 h	120 h	192 h	240 h	360 h
NaCl	15.416 ± 0.72	47.125 ± 0.45	84.166 ± 1.19	139.666 ± 2.76	176.666 ± 11.1	278.333 ± 7.20
KCl	14.916 ± 0.44	44.833 ± 0.52	79.166 ± 0.48	137.916 ± 5.75	170.333 ± 5.40	269.166 ± 6.62
Na_2SO_4	6.499 ± 0.28	27.249 ± 0.08	52.249 ± 1.26	87.493 ± 2.42	119.499 ± 9.20	171.666 ± 4.46
CaCO_3	5.249 ± 0.18	19.499 ± 2.43	31.916 ± 0.96	42.833 ± 0.83	53.416 ± 2.78	67.083 ± 1.04
CaCl_2	2.916 ± 0.05	13.166 ± 0.08	29.083 ± 0.08	68.833 ± 1.24	73.166 ± 1.54	89.666 ± 3.16
MgSO_4	3.083 ± 0.02	13.500 ± 0.05	25.500 ± 0.28	47.666 ± 0.30	60.583 ± 0.30	79.916 ± 3.42
NaHCO_3	5.916 ± 0.28	25.416 ± 0.64	42.500 ± 1.50	56.416 ± 1.14	69.750 ± 2.76	89.666 ± 3.16
NaNO_3	1.249 ± 0.00	5.249 ± 0.02	10.499 ± 0.50	17.499 ± 0.58	21.917 ± 0.60	39.583 ± 0.30
MnSO_4	0.000 ± 0.00	0.416 ± 0.06	1.499 ± 0.05	4.000 ± 0.62	6.749 ± 0.12	9.749 ± 0.36
$\text{Pb}(\text{NO}_3)_2$	0.000 ± 0.00	0.583 ± 0.01	3.000 ± 0.01	4.083 ± 0.18	4.499 ± 0.44	4.499 ± 0.42
KBr	0.083 ± 0.01	3.333 ± 0.12	5.666 ± 0.20	9.749 ± 0.03	12.49 ± 0.78	19.416 ± 0.82
KI	0.083 ± 0.01	3.000 ± 0.16	5.000 ± 0.53	9.166 ± 0.57	11.916 ± 0.76	18.666 ± 0.68
Composite water	67.416 ± 2.66	210.583 ± 9.37	368.333 ± 11.15	598.083 ± 14.72	761.583 ± 17.17	1146.080 ± 22.46

cast iron for different durations of exposure in different aqueous salt solutions. An increase in value of loss in weight was observed. The corrosion of cast iron in various aqueous salt solutions was in the order of $A > B > C > G > D > F > E > H > L \cong K > J \cong I$ for 24 h, $A > B > C > G > D > F > E > H > L > K > J > I$ for 72 h, $A > B > C > G > D > E > F > H > L > K > J > I$ for 120 h, $A > B > C > E > G > F > D > H > K > L > J > I$ for 192 h, $A > B > C > E > G > F > D > H > K > L > I > J$ for 240 h and $A > B > C > E \cong G > F > D > H > K > L > I > J$ for 360 h. Although for all durations order of variation in corrosion rate of cast iron remains the same for NaCl, KCl, Na_2SO_4 , NaNO_3 , however, it changes significantly for CaCO_3 , CaCl_2 , MgSO_4 , NaHCO_3 , MnSO_4 , $\text{Pb}(\text{NO}_3)_2$, KBr and KI. The two anions that are reported to have a significant influence on the corrosion characteristics of cast iron are chloride and sulphate ions. The relative increase is 0.204 times for NaCl, 0.203 times for KCl, 0.761 times for Na_2SO_4 , 0.148 times for CaCO_3 , 1.049 times for CaCl_2 , 0.728 times for MgSO_4 , 0.010 times for NaHCO_3 , 1.111 times for NaNO_3 , 0.130 times for MnSO_4 , 0.060 times for $\text{Pb}(\text{NO}_3)_2$, 14.556 times for KBr, 13.958 times for KI from 24 h to 360 h duration. The relative increase in corrosion rate is less because of neutral or slightly basic nature of salts (Foley 1978). The major effect on cast iron

is due to adsorption behaviour of anions of the electrolyte at the electrode surface.

It is clear from table 2 that metal loss increases progressively with time solutions but corrosion rate does not follow a definite trend for all test solutions and is not proportional with time, solutions being of different nature and present in different concentrations. The corrosion rate of cast iron in NaCl, KCl, Na_2SO_4 , CaCl_2 , NaNO_3 , MnSO_4 , KBr, KI increase continuously with immersion period while in the CaCO_3 , MgSO_4 , NaHCO_3 and $\text{Pb}(\text{NO}_3)_2$ test solutions the corrosion rate increase is followed by a decrease after some period. This may be because of anions accelerator and inhibitor behaviour caused by stability of ferric oxide film formed after corrosion reaction. The relative increase in halide ions salts is found to be more than other ions because of corrosive nature of halide ions than sulphate and nitrate ions.

The initial rate of corrosion is high for NaCl and KCl and the relative increase in corrosion rate is less as the reaction proceeds, because there remains no direct contact between metal surface and corrosive ions by corrosion product and excess of cations nearby the metal surface. On the other hand in the KBr and KI test solutions the initial corrosion rate is less due to non availability of anions at the metal surface. After initiation of reaction,

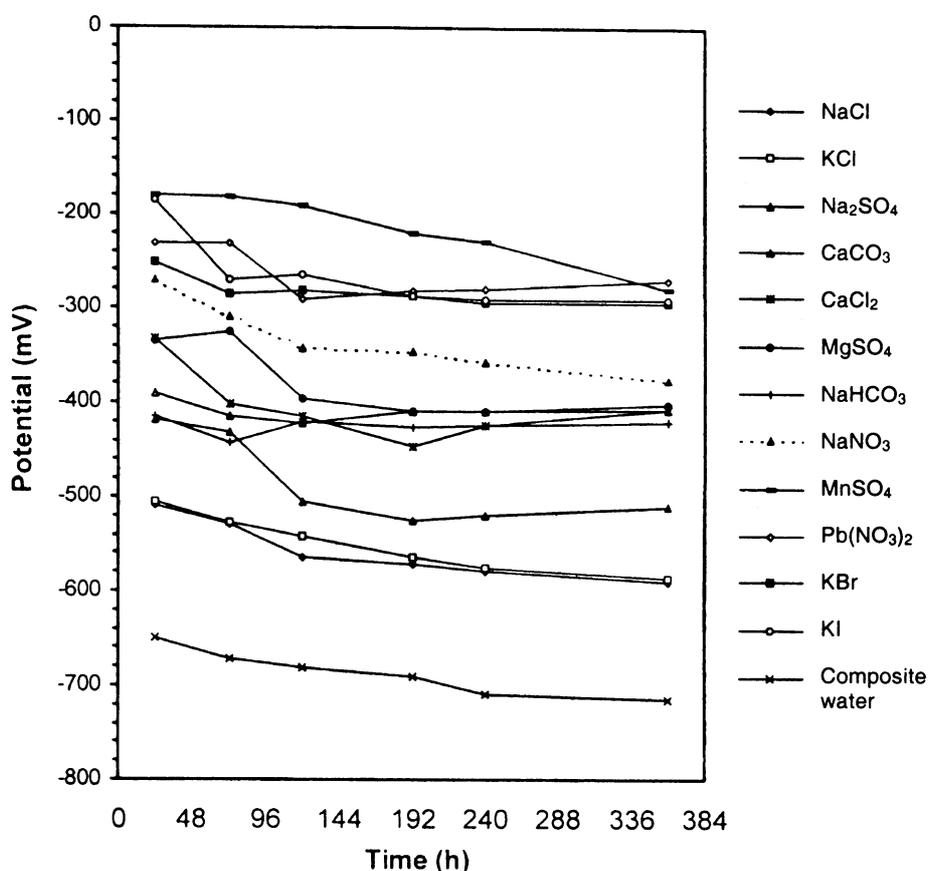


Figure 1. Potential vs time curves for cast iron in different test solutions and composite water.

the rate increases continuously and is not hindered by corrosion as in the case of KCl, NaCl and CaCl₂. The negative increase in CaCO₃ and less increase in NaHCO₃ of corrosion rate indicates the non corrosive behaviour of CaCO₃ and NaHCO₃ because of less mobility of Ca²⁺ and HCO₃⁻ ions (Chandra *et al* 1994; Hammout *et al* 1995). These results cannot be compared with earlier studies as they correspond to high anionic concentrations. The average contribution of these salts to corrosion rate in potable water is 24.20% for NaCl, 23.32% for KCl, 14.15% for Na₂SO₄, 7.98% for CaCO₃, 8.14% for CaCl₂, 7.04% for MgSO₄, 10.22% for NaHCO₃, 2.83% for NaNO₃, 0.50% for MnSO₄, 0.46% for Pb(NO₃)₂, 1.39% for KBr and 1.29% for KI from 24 h to 360 h duration of immersion.

The specimens immersed in the different test solutions develop the open circuit potential as -590 mV for NaCl, -587 mV for KCl, -512 mV for Na₂SO₄, -408 mV for CaCO₃, -408 mV for CaCl₂, -402 mV for MgSO₄, -420 mV for NaHCO₃, -376 mV for NaNO₃, -227 mV for MnSO₄, -280 mV for Pb(NO₃)₂, -295 mV for KBr, -290 mV for KI, -715 mV for composite water. The

variation of OCP with time have been given in figure 1, which depicts an inverse relationship with corrosion rate. The OCP in all test solutions regardless of their nature, shift towards negative (less noble) direction with the passage of immersion period and finally attain steady state in ~360 h. Further, figure 1 shows that steady state potential for different test solutions are in the order A < B < G < E ≅ D < H < K < L < J < I which support the corrosion rate order for 360 h duration of immersion.

Anodic and cathodic polarization plots for cast iron in different test solutions are furnished in figure 2. The values of I_{corr} , Tafel slopes and OCP for various test solutions calculated from polarization curves have been given in table 3. Tafel curves show higher values for cathodic slopes than anodic due to the dissolution of anode into the test solution. The order of corrosion rate for cast iron in different test solutions observed by weight loss and potentiostatic polarization method is in good agreement but the corrosion rate calculated from potentiostatic method are higher than calculated from weight loss method. This is expected since corrosion rate is maximum in the beginning and decreases when

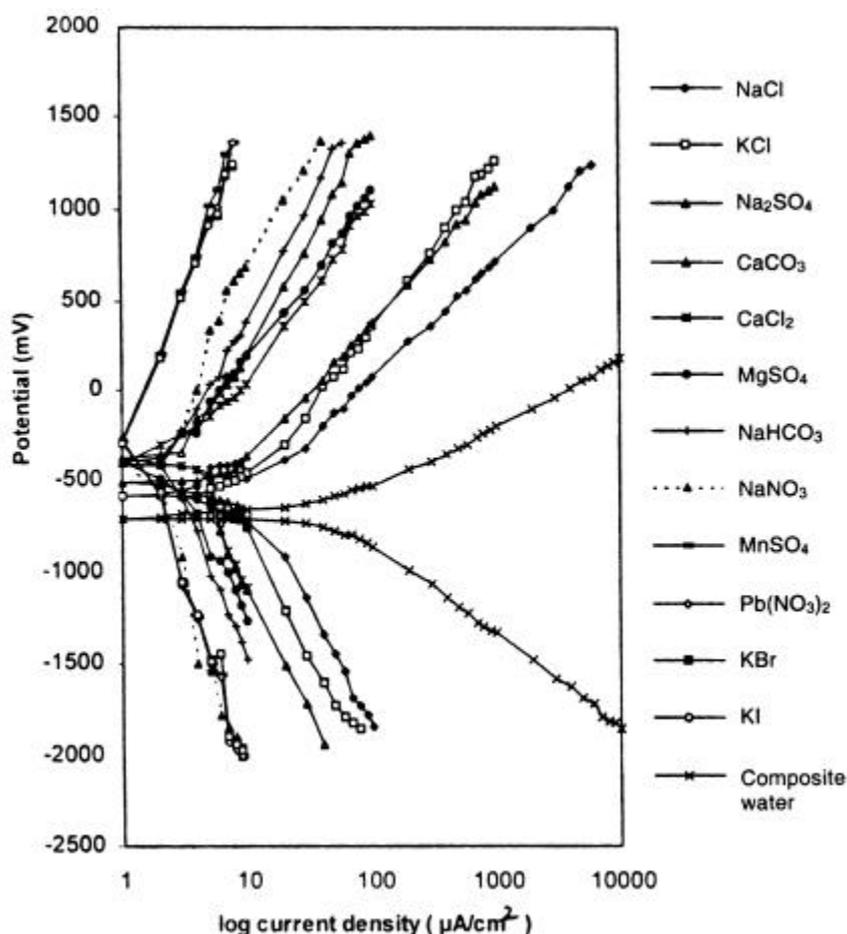


Figure 2. Potentiostatic polarization curves for cast iron in different test solutions and composite water for 360 h.

Table 3. Potentiostatic parameters for cast iron in different test solutions after 360 h duration of exposure at $28 \pm 1^\circ\text{C}$.

Solution	OCP (- mV)	$I_{\text{corr.}}$ (μA)	ba (mV/decade)	bc (mV/decade)	Corr. rate from polari. data (mmpy)	Corr. rate from wt. loss data (mmpy)
KCl	- 590	11.220	58	120	0.144	0.095
NaCl	- 587	10.960	62	127	0.141	0.092
Na_2SO_4	- 512	6.607	84	128	0.085	0.058
CaCO_3	- 408	2.138	88	125	0.027	0.023
CaCl_2	- 408	3.631	88	125	0.046	0.030
MgSO_4	- 402	2.692	75	140	0.034	0.027
NaHCO_3	- 420	2.951	96	140	0.038	0.030
NaNO_3	- 376	1.479	120	140	0.019	0.013
MnSO_4	- 280	0.316	168	190	0.004	0.003
$\text{Pb}(\text{NO}_3)_2$	- 270	0.126	160	170	0.002	0.002
KBr	- 295	0.794	160	190	0.010	0.0065
KI	- 290	0.794	160	194	0.010	0.0063
Composite water	- 715	58.88	36	52	0.756	0.389

equilibrium value is attained. But in contradiction to the previous studies (Smith 1980; Singh and Rao 1998), the corrosion rates obtained from potentiostatic measurements are not significantly high than those by weight loss measurements. Even in CaCO_3 the corrosion rates are nearly similar. These observed results can be correlated with the small concentration of ions and small values of corrosion rates as compared to earlier studies (Koshel *et al* 1988).

According to Fontana for the more commonly used low C steel and steel alloy, < 1 mpy is outstanding corrosion rate, 1–5 mpy is excellent, 5–20 mpy is good and can be used with caution, 20–50 mpy is fair and can be used for short exposure, 50–200 mpy is poor and above 200 ppm completely unacceptable (Fontana 1986; Mehra and Soni 2002). However, these corrosion rates calculated are acceptable for long exposure. But the corrosion rates are due to a significant contribution of all salts available in water, hence best promising results can be obtained by decreasing corrosion due to each of the salt.

4. Conclusions

From the above results it is clear that anions play a decisive role in determining the ease with which cast iron undergoes dissolution upon application of some anodic current density. The order of corrosion in various salt solutions is $A > B > C > G > D > F > E > H > L \cong K > J \cong I$ for 24 h, and $A > B > C > E \cong G > F > D > H > K > L > I > J$ for 360 h, i.e. halide ions contribute significantly to the corrosion rate of cast iron in potable water, sulphate and nitrate ions have intermediate effect and carbonate and bicarbonate have minimum contribution to corrosion of cast iron in potable water. Excellent corrosion resistance in the present investigation can be further upgraded to outstanding corrosion rate by inhibiting corrosion by

72.24% for NaCl, 73.15% for KCl, 56.47% for Na_2SO_4 , 00.00% for CaCO_3 , 16.67% for CaCl_2 , 6.51% for MgSO_4 , 16.65% for NaHCO_3 , 00.00% for NaNO_3 , 00.00% for MnSO_4 , 00.00% for $\text{Pb}(\text{NO}_3)_2$, 00.00% for KBr and 00.00% for KI individually. To decrease the corrosion rate of cast iron in composite potable water to an excellent corrosion resistance, the corrosion should be decreased by 67.40% using appropriate check measures and inhibitors.

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