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Short communication

Stability of perchlorate ions in acid medium: Interaction with zinc and aluminium

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Introduction

In a previous communication [1] the problem of the stability of perchlorate ions in acid medium at solid–liquid interfaces was surveyed and, as new evidence, their interaction with nickel and copper was reported. Although the reduction of perchlorate ions at various electrodes might be very slow, the possible role of this process, primarily the role of Cl^- ions formed in the reduction process, cannot be neglected in most kinetic and mechanistic studies. The same previous communication also shows that a simple analysis of the solution in contact with the corresponding metal under open circuit conditions can furnish information on the interaction of perchlorate ions with the metal. As almost in all cases, where the reduction of perchlorate ions was observed, Cl^- was the main reduction product the analysis may be restricted to this species.

The intention of the present communication is to show that the spontaneous corrosion of zinc and aluminium in the presence of perchloric acid is accompanied by the reduction of perchlorate ions leading to the formation of chloride ions.

2. Experimental details

Similarly to the procedure described in the previous communication [1] the formation of Cl^- ions was followed by potentiometric titration using a silver chloride electrode (detection limit: 2×10^{-5} M Cl^-). Analytical grade (99.99%) metals and chemicals were used. The measurement of the Cl^- concentration was combined with the determination of the amount of metal consumed, measuring the mass of the metal before and after the corrosion. This procedure enabled us to estimate the grade of conversion of the metal with respect to the anion reduction.

Similarly to the previous communication, observations made in the presence of ClO_4^- and ClO_3^- were compared in order to show that the transformation of ClO_4^- into ClO_3^- ion is the slowest step in the process leading to the formation of Cl^-. The volume of the solution phase was generally 50 ml. In the case of the ClO_3^- addition the final volume was 55 ml.

3. Results and discussion

3.1. *Aluminium*

There is evidence in the literature suggesting the interaction of ClO_4^- ions with Al. For instance, the reduction of ClO_4^- ions was observed in a combined potentiostatic and photoelectron spectroscopy (ESCA) study of the formation and breakdown of the passivating film on aluminium [2]. A considerable amount of Cl^- ions was found in the oxide layer in the case of 0.1 M ClO_4^- ions in the solution phase, containing 0.33 M $Al_2(SO_4)_3$ supporting electrolyte.

It was assumed that the reduction process is preceded by the adsorption of ClO_4^- ions and the reaction takes place at the oxide film/solution interface. In connection with the reaction path suggested by Painot and Augustynski [2] it should be mentioned that recent studies concerning the specific adsorption of sulfate ions on aluminium oxides in the presence of a large excess of ClO_4^- ions do not justify the assumption that ClO_4^- ions can adsorb to a significant extent in the presence of an excess of sulfate ions [3]. Nevertheless, to our knowledge, there have been no reports of the appearance of Cl^- ions in the solution as a consequence of ClO_4^- reduction in the course of the corrosion of aluminium.

The data presented in Table 1 show, without any doubt, that the reduction of ClO_4^- ions in acidic solution, according to the overall process $ClO_4^- + 8H^+ + 8e^- = Cl^- + 4\,H_2O$, despite its slowness, cannot be neglected in corrosion studies of aluminium carried out in the presence of ClO_4^- ions. Presumably, the reduction process takes place stepwise through chlorate; therefore, the reduction rate of chlorate ions was also considered. Data presented in Table 1 demonstrate that

Table 1. Interaction of Al (5×10^{-3} mol) with ClO_4^- and ClO_3^- ions at $T = 25$ °C

Electrolyte	*A* (amount of dissolved Al) /mol	Addition	Contact time /days	c_{Cl} /M	*B* (Cl^- formed) /mol	*B* /*A*	Conversion /%
1 M $HClO_4$	2.89×10^{-3}	0	17	2.41×10^{-4}	1.21×10^{-5}	4.19×10^{-3}	1.1
1 M $HClO_4$	2.82×10^{-3}	0	17	3.41×10^{-4}	1.71×10^{-5}	6.06×10^{-3}	1.6
1 M $HClO_4$	1.22×10^{-3}	2 M $NaClO_4$	7	5.08×10^{-4}	2.79×10^{-5}	2.29×10^{-2}	6.1
1 M $HClO_4$	1.56×10^{-3}	2 M $NaClO_4$	7	3.85×10^{-4}	1.93×10^{-5}	1.24×10^{-2}	3.3
1 M $HClO_4$	4.15×10^{-3}	5×10^{-1} M $NaClO_3$	7	1.54×10^{-2}	8.47×10^{-4}	2.04×10^{-1}	54
0.5 M H_2SO_4	8.52×10^{-4}	5×10^{-1} M $NaClO_3$	7	3.08×10^{-3}	1.69×10^{-4}	1.98×10^{-1}	52

Table 2. Interaction of Zn (6.5×10^{-3} mol) with ClO_4^- and ClO_3^- ions at $T = 25$ °C

Electrolyte	*A* (amount of dissolved Zn) /mol	Addition	Contact time	c_{Cl^-} /M	*B* (Cl^- formed) /mol	*B* /*A*	Conversion /%
1 M $HClO_4$	4.76×10^{-3}	0	7 days	3.51×10^{-4}	1.76×10^{-5}	3.70×10^{-3}	1.5
1 M $HClO_4$	5.95×10^{-3}	0	17 days	5.43×10^{-4}	2.72×10^{-5}	4.57×10^{-3}	1.8
1 M $HClO_4$	5.90×10^{-3}	0	17 days	3.91×10^{-4}	1.96×10^{-5}	3.32×10^{-3}	1.3
1 M $HClO_4$	6.07×10^{-3}	2 M $NaClO_4$	7 days	2.80×10^{-4}	1.54×10^{-5}	2.54×10^{-3}	1.0
1 M $HClO_4$	6.42×10^{-4}	0	30 min	$<10^{-5}$			
1 M $HClO_4$	6.29×10^{-3}	5×10^{-1} M $NaClO_3$	30 min	3.09×10^{-2}	1.70×10^{-3}	2.70×10^{-1}	81.0
0.5 M H_2SO_4	5.88×10^{-3}	5×10^{-1} M $NaClO_3$	30 min	2.66×10^{-2}	1.46×10^{-3}	2.48×10^{-1}	74.4

the reduction rate of ClO_3^- ions is higher than that of ClO_4^-; however, it is surprising that the difference between the rates of the two reactions is not so pronounced as in the case of Ni, Cu [1] and Zn (see later). Nevertheless, in the presence of ClO_3^- about 50–55% of the Al metal dissolved is consumed in the reaction with the anion and this value is more than one order of magnitude higher than that observed in the presence of ClO_4^- ions. (Of course, the results presented do not provide a definitive proof that ClO_3^- is an intermediate of the reduction of ClO_4^-.) It is also remarkable that addition of ClO_4^- ions in the form of $NaClO_4$ results in an increase in the conversion. On the other hand it is interesting that, in the presence of sulfuric acid, the reduction of ClO_3^- ions is inhibited to some extent although the conversion of the metal in the presence of $HClO_4$ and H_2SO_4 is practically the same.

3.2. *Zinc*

Table 2 summarizes the results of experiments carried out with Zn powder. The conversion degree of ClO_4^- ions into Cl^- ions is about 1–2%, similar to the value found for Al. However, the rate of ClO_3^- reduction is several orders of magnitude higher that that of ClO_4^- ions. In addition, the conversion attains 70–80%. In contrast to the observation made in the case of Al the increase in ClO_4^- concentration by addition of $NaClO_4$ does not exert significant influence on the reduction rate of ClO_4^- ions.

4. Conclusions

The simple experimental procedures described here furnish unambiguous evidence concerning the reduction of ClO_4^- ions at Al and Zn–electrolyte interfaces in acid medium. The corrosion processes of these metals in solutions containing ClO_4^- ions cannot be discussed without taking into consideration the role of the possible reduction processes and the possible influence of the reduction product, Cl^- ions.

From the mechanistic point of view it is important to emphasize that, similarly to the case of Ni and Cu [1], the comparison of the interaction of ClO_3^- and ClO_4^- ions with Al and Zn suggests that the perchlorate → chlorate transformation should be the rate determining step in the overall reduction of ClO_4^- ions.

Considering the high conversion values of the metals for the interaction with ClO_3^- ions these latter species should be considered as very aggressive corrosion agents, even at low concentration.

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