

Short communication

Metal elution from Ni- and Fe-based alloy reactors under hydrothermal conditions

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Abstract

Elution of metals from Ni- and Fe-based alloy (i.e. Inconel 625 and SUS 316) under hydrothermal conditions was investigated. Results showed that metals could be eluted even in a short contact time. At subcritical conditions, a significant amount of Cr was extracted from SUS 316, while only traces of Ni, Fe, Mo, and Mn were eluted. In contrast, Ni was removed in significant amounts compared to Cr when Inconel 625 was tested. Several factors including temperature and contact time were found to affect elution behavior. The presence of air in the fluid even promoted elution under subcritical conditions.

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1. Introduction

The utilization of high-temperature and high-pressure water in various organic reactions is of interest to researchers. Water at subcritical conditions, due to its high ion product, could be a good solvent for the recovery of useful materials from various natural wastes [1,2] as well as for organic synthesis [3–5]. Supercritical water provides rapid and complete oxidation for the destruction of hazardous materials or organic wastes [6,7]. The technology seems to be promising for resource recovery and wastewater treatment processes. However, problems such as corrosion of the surface of reactor vessel accompany the use of high-temperature and high-pressure water [8]. This corrosion would result in the elution of heavy metals into the reaction media. The presence of heavy metals in the product is not desirable both from an environmental and health viewpoint, especially if the products are intended for human consumption. Although studies had been done on corrosion of various types of materials in the past [9–13], it is also important to quantify

the presence of heavy metals in reaction media during hydrothermal treatment process.

The above reason motivated us to study metal elution of the commonly used metal alloys (i.e. Ni-based Inconel 625 and Fe-based SUS 316) under hydrothermal conditions. As a preliminary study, only water was used with no particular reaction being considered. Although corrosion studies are normally conducted for long time, this study focused on metal elution occurring in a short contact time between the reaction media and the metal surface. The reason for use of this time period is that most hydrothermal processes are economically feasible only if operated for a short period considering the required energy. We also investigated the affect of various parameters such as temperature and time and the affect of the presence of air on the amount of eluted metals. The role of chromium protective layers on the amount of eluted metal in the product are also discussed.

2. Experimental

Two types of materials were utilized in this study—Inconel 625 and SUS 316. Inconel 625 is a Ni-based alloy consisting of 60% Ni, 20% Cr, 9% Mo, and 5% Fe. SUS 316 is Fe-based consisting of 65% Fe, 18% Cr, 12% Ni, 2% Mo, and 1% Mn. In each experimental run, tubular metal samples (Inconel 625, i.d. = 0.68 cm, L = 70 cm; SUS

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316, i.d. = 0.025 cm, $L = 2000$ cm) were connected to the high-temperature and high-pressure apparatus described in details elsewhere [1].

Deionized water was introduced into the tubular reactor by an HPLC pump, and the flowrate was adjusted to obtain a residence time of 30–600 s. Experiments on the effect of temperature were performed over the range of 250–400 °C, while maintaining the pressure at 25 MPa. Deionized water was degassed using an ultrasonic wave (CA-4488R, Kaijo Corp.) and handy aspirator (Model WP 15, Yamato Scientific Co. Ltd.). The affect of the presence of air was also investigated by comparing the results of using degassed and non-degassed deionized water. The concentration of eluted metals was measured using inductively coupled plasma (ICP) atomic emission spectrometer (SPS 7700R, Seiko Instrument Inc.)

3. Results and discussion

3.1. Temperature-dependence of metal elution

Fig. 1 shows the effect of temperature on the amount of eluted metal from the two metal samples for a residence time of 30 s. The amount of eluted metal is expressed in terms of contact area between the fluid and the metals. Results showed that a significant amount of metal is eluted at subcritical conditions, due likely to the high ion product of water, compared to its lower concentration at supercritical conditions. Our results agree with previous findings on corrosion behavior [11–15].

In general, Cr and Mo are mainly eluted at subcritical conditions compared to elution at supercritical conditions. This result is likely due to the formation of a chromium protective layer at high temperatures. Elution of Fe (in the case of SUS 316) and Ni (in the case of Inconel 625) increases with increasing temperature. We also found that Fe is a fairly stable compared to Ni. The amount of eluted metals from SUS 316 is relatively higher compared to that of Inconel 625 at all conditions.

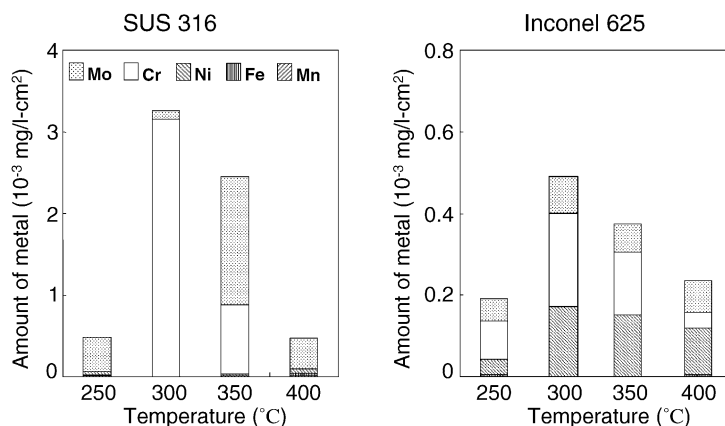


Fig. 1. Temperature dependence of the amount of metal eluted from SUS 316 and Inconel 625 (contact time = 30 s).

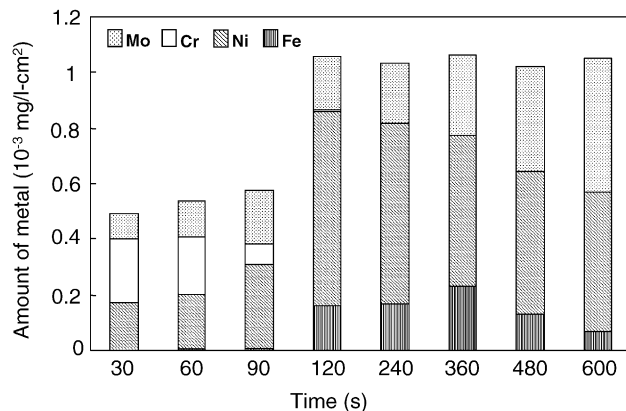


Fig. 2. Effect of contact time on the amount of metal eluted from Inconel 625 ($T = 300$ °C).

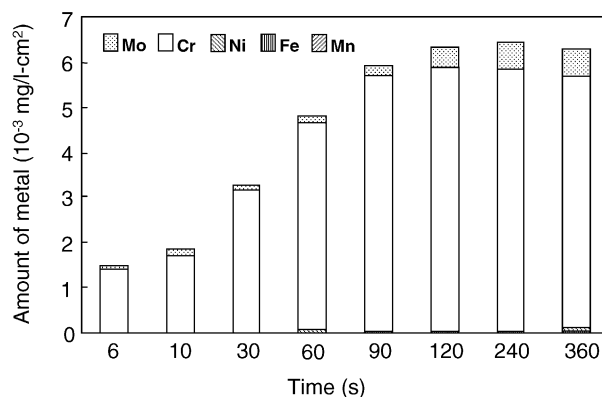


Fig. 3. Effect of contact time on the amount of metal eluted from SUS 316 ($T = 300$ °C).

3.2. Effect of contact time between metal and fluid

Metal elution is also dependent on the contact time between the metal and the fluid. Consequently, we measured the impact of residence time on elution at 300 °C. Figs. 2 and 3 show that the amount of eluted metal, from both Inconel 625 and SUS 316 increased with increasing contact

time but reaches a limit. However, the diverse metal concentration changes.

In case of Inconel 625, Cr decreases with increasing time as shown in Fig. 2. This decrease in the eluted ion is most likely due to complete formation of a protective oxide layer. The amount of eluted Ni, the major component of Inconel 625, increases with increasing contact time up to 240 s then thereafter becomes stable. It is likely that Ni reacts with Cr, which promotes the formation of protective layers of NiCr_2O_4 . Mo, which improves the resistance of alloys to non-oxidizing acids [16], increases with increasing time resulting to selective dissolution of Mo. Fe starts eluting at a contact time of 90 s and increases with time.

In case of SUS 316, Cr is the most dominant metal eluted and the same trend was observed even at longer residence times. Mo, was also detected in the extraction fluid and increased with increasing time. Fig. 3 also shows that only small amount of Ni, Mn, and Fe were eluted. Ni decreases with increasing elution time. Mn, a minor component, was also detected and increased with increasing time.

Mn, even in small amounts, may affect the properties of the chromia scale [9]. The presence of this element is beneficial considering that MnO may react with Cr_2O_3 to form protective layers of MnCr_2O_4 . Fe, the major component of SUS 316, increases with increasing time.

The elution behavior at other temperatures may not exhibit the same trend as that at 300 °C. Table 1 summarizes the results of the behavior of metal elution from SUS 316 and Inconel 625 at various conditions.

3.3. Effect of the presence of air on metal elution

Air in the fluid may affect the elution. Thus, experiments were performed on SUS 316 in the presence of air. Results in Fig. 4 show that at subcritical conditions ($T = 250\text{--}350\text{ }^\circ\text{C}$), the amount of eluted metal is higher in the presence of air than in its absence. It is likely that oxygen promotes metal as anodic oxidation process. At 400 °C, however, the elution especially of Fe is favorable in the absence of air. This be-

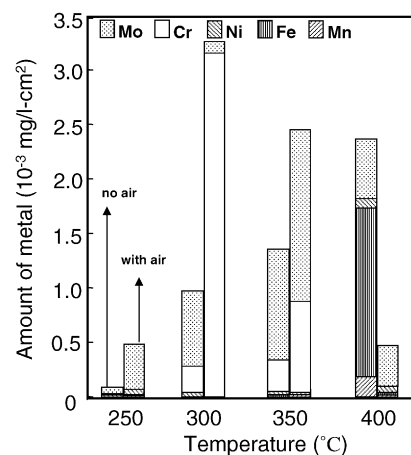


Fig. 4. Effect of air on the amount of metal eluted at various temperatures (SUS 316, contact time = 30 s).

havior is most likely due to the relatively high concentration of H^+ ions in the absence of O_2 , a condition which lowers the resistance of Fe. In this regard, it was also observed that elution of Fe is favorable under acidic conditions.

3.4. Role of chromium

Cr is an important component of metal alloys in resisting corrosion at elevated temperatures. The formation of Cr-protective layers in the process could be the reason for the varying amount of eluted Cr at various times and temperatures. The low concentration of Cr detected at 400 °C, does not agree with the previous findings of Carranza and Alvarez [10] indicating that the passive film was found to be more porous, and hence less protective as the temperature increased.

The amount of Cr in metals, indeed, has an effect on elution. Results show that Inconel 625, which contains more Cr than SUS 316, is more corrosion-resistant than SUS 316. This finding agrees with the previous results of other researchers [11,17]. In addition, the amount

Table 1
Summary of the results of metal elution from SUS 316 and Inconel 625 at various temperatures

| Material and conditions | Components | | | | |
|-------------------------|---------------|----------------|---------------|----------------|----|
| | Mo | Cr | Ni | Fe | Mn |
| SUS316 | | | | | |
| 250 °C | -- | ND | -- | -- | ± |
| 300 °C | ++ | ++ | -- | ++ | ++ |
| 350 °C | ++ | -- after 240 s | -- | -- | ++ |
| 400 °C | -- | ND | ± | ++ | -- |
| Inconel 625 | | | | | |
| 250 °C | ++ | -- after 240 s | ++ | -- after 240 s | |
| 300 °C | ++ | ND after 120 s | ± after 240 s | -- after 360 s | |
| 350 °C | ++ | -- | ± after 120 s | ND | |
| 400 °C | ± after 120 s | -- | ++ | ND | |

++: increases with increasing time; ND: below detection limit of ICP; --: decreases with increasing time; ±: stable.

of eluted metals is relatively higher when new metal is used compared to the old one, especially in the case of SUS 316.

3.5. Environmental and health impact

The presence of eluted metals in the product is not desirable both on the viewpoint of environment and health. In a hydrothermal process for wastewater treatment, the presence of trace amounts of metals has no significant effect as long as these concentration meet government limits on wastewater quality. However, if the products are intended for human consumption, the presence of even trace amounts of metals may be hazardous. For example, the presence of Cr(VI) above 0.05 mg/l can cause serious health problems such as cancer. In this regard, Gloyna and Li [14] detected traces of Cr(VI) in the effluent of hydrothermal treatment of sludge.

In this study, a significant amount of Cr was detected at subcritical conditions. The total Cr eluted from SUS 316 is over the WHO limit for drinking water [18]. The eluted Cr from Inconel 625 did not exceed the acceptable level.

However, the concentrations of Mo from SUS 316 at 350 °C and Ni from Inconel 625 at 300 °C were over the acceptable level. Fe and Mn eluted from both metals were below the level. However, this result is likely to increase under acidic conditions.

4. Conclusion

Elution of heavy metals occurred under hydrothermal conditions even in a short contact time between the metal and the reaction media. The amount of eluted metal is higher at subcritical conditions than at supercritical conditions. At 300 °C, the eluted metal from SUS 316 contained significant amounts of Cr and traces of Ni, Fe, Mo, and Mn. In contrast, in the case of Inconel 625, significant amounts of Ni but only traces of Cr were detected. Elution was found to be dependent in temperature and contact time. It was also observed that the presence of air promotes elution under subcritical conditions.

The above results are useful in evaluating the use of hydrothermal treatment process for waste treatment and resource recovery.

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References

- [1] K. Kang, A.T. Quitain, H. Daimon, R. Noda, N. Goto, H. Hu, K. Fujie, *Can. J. Chem. Eng.* 79 (2001) 65–70.
- [2] A. Shanableh, *Water Res.* 34 (2000) 945–951.
- [3] T.J. Houser, X. Liu, *J. Supercrit. Fluids* 9 (1996) 167–171.
- [4] P.E. Savage, *Chem. Rev.* 99 (1999) 603–621.
- [5] R.L. Holliday, B.Y.M. Jong, J.W. Kolis, *J. Supercrit. Fluids* 12 (1998) 255–260.
- [6] M. Goto, T. Nada, S. Kawajari, A. Kodama, T. Hirose, *J. Chem. Eng. Jpn.* 30 (5) (1997) 813–818.
- [7] M. Goto, T. Nada, A. Ogata, A. Kodama, T. Hirose, *J. Supercrit. Fluids* 13 (1998) 277–282.
- [8] R.W. Shaw, T.B. Brill, A.A. Clifford, C.A. Eckert, E.U. Franck, *Chem. Eng. News* 12 (1991) 26–38.
- [9] P. Kofstad, *High Temperature Corrosion*, Elsevier, New York, England, 1988, p. 529.
- [10] R.M. Carranza, M.G. Alvarez, *Corros. Sci.* 38 (1995) 909–925.
- [11] P. Kritzer, N. Boukis, E. Dinjus, *J. Supercrit. Fluids* 15 (1999) 205–227.
- [12] R.M. Latanision, D.B. Mitton, S.H. Zhang, J.A. Cline, N. Caputy, T.A. Arias, A. Rigos, in: *Proceedings of the 4th Symposium on Supercritical Fluids*, Senday, Japan, May 1997.
- [13] S.Y. Kim, D.B. Mitton, R.M. Latanision, *Korean J. Chem. Eng.* 17 (2000) 58–66.
- [14] E.F. Gloyna, L. Li, *Waste Manag.* 13 (1993) 379–394.
- [15] P. Kritzer, N. Boukis, E. Dinjus, *Corrosion* 98, Paper No. 415, San Diego, CA, 1998.
- [16] D.S. Anderson, D.B. Craig, *Handbook of Corrosion Data*, ASM International, Materials Park, USA, 1995.
- [17] D.B. Mitton, J.H. Yoon, J.A. Cline, H.S. Kim, N. Eliaz, R.M. Latanision, *Ind. Eng. Res.* 39 (2000) 4689–4696.
- [18] World Health Organization, *Guidelines for Drinking-Water Quality*, vol. 2, Austria, 1996, pp. 206–308.