THE BEHAVIOR OF SOLUBLE METALS ELUTED FROM Ni/Fe-BASED ALLOY REACTORS AFTER HIGH-TEMPERATURE AND HIGH-PRESSURE WATER PROCESS

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Abstract

The behavior of heavy metals eluted from the wall of Ni/Fe-based alloy reactors after high-temperature and high-pressure water reaction were studied at temperatures ranging from 250 to 400°C. For this purpose, water and cysteic acid were heated in two reactor materials which are SUS 316 and Inconel 625. Under the tested conditions, the erratic behaviors of soluble metals eluted from the wall of Ni/Fe-based alloy in high temperature water were observed. Results showed that metals could be eluted even at a short contact time. The presence of air also promotes elution at sub-critical conditions. At sub-critical 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. It was observed that eluted metals tend to increased under acidic conditions and most of those metals were over the limit of WHO guideline for drinking water. The results are significant both on the viewpoint of environmental regulation on disposal of wastes containing heavy metals, toxicity of resulting product and catalytic effect on a particular reaction.

Keywords: environmental; high-temperature and high-pressure water; metal elution; Ni/Fe-based alloy; reactor materials
INTRODUCTION
The field of high-temperature and high-pressure (HTHP) water reaction is of great scientific and technological importance, and it has been a growing interest and an active field of research for several years. This process has been found as a promising medium for a large number of processes. At subcritical conditions water has been found to be a medium for recovery of useful materials from organic wastes (Faisal et al., 2005; Kang et al., 2001; Shanableh, 2000; Yoshida et al.; 1999) and organic synthesis (Faisal et al., 2008a, Faisal et al., 2008b; Faisal et al., 2007; Houwer and Liu, 1996; Savage, 1999; Holliday et al., 1998) due to its high-ion product. Supercritical water provides rapid and complete oxidation for destruction of organic wastes (Goto et al., 1997 and Goto et al., 1998). The dramatic decreases in solvent viscosity, increase in substrate solubility, and enhance sensitivity of solvating properties of the supercritical fluid to temperature and pressure make them attractive as potential solvent (Holliday et al., 1998). Strong temperature dependence of the properties provides opportunities to tune the reaction environment to optimal conditions for the chemical transformation of interest (Shaw et al., 1991). 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 HTHP water process (Kofstad, 1998). This corrosion would result in the elution of soluble heavy metals into the reaction media. The presence of those 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 has been done on corrosion of various types of materials in the past (Carranza and Alvarez, 1995; Kritzer et al., 1999; Latanision et al., 1997; Kim et al., 2000 and Gloyna et al., 1993), it is also important to quantify the presence of heavy metals in reaction media during HTHP process. Reactor materials and reaction conditions could greatly influence the behavior of metal elution. Besides, the elution mechanism occurring under such conditions is still unclear. This behavior must be clearly understood prior to building full scale operational plant.

Therefore study on the behavior of soluble metals of the commonly used metal alloys (i.e. Ni-based Inconel 625, and Fe-based SUS 316) under HTHP process is of great important. 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 elution of metals under hydrothermal conditions in a short communication had been reported (Faisal et al., 2004). The reason for used of this time period is that most HTHP processes are economically feasible only if operated for a short period considering the required energy.

In this study, the amount of metals eluted from Inconel 625 and SUS 316 is investigated and the influence of various conditions on metal elution is explored. This includes investigation of the effect of temperature and time on metal elution, the role of chromium protective layers and environmental effect of the presence of eluted metal in the desired product are also discussed in this work. The results are significant both on the viewpoint of environmental regulation on disposal of waste containing heavy metals and toxicity of resulting product. Thus might contributes to developing of this technique toward engineering and process design.

RESEARCH METHOD
Experimental Apparatus and Method
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, ID=0.68 cm, L=70 cm; SUS 316, ID=0.025 cm, L=2000 cm) were connected to the high-temperature and high-pressure apparatus described in details elsewhere (Faisal et al., 2008a). Deionized water was introduced into the tubular reactor by an HPLC pump, and the flow rate was adjusted to obtain a residence time of 30 to 600s. Experiments on the effect of temperature were performed over the range of 250 to 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.

Analysis
The amount of eluted metals was measured using Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer (SPS 7700R, Seiko Instrument Inc.) Since the initial sample for ICP analysis was de-ionized water, no pre-treatment was carried out except for the analysis of hexavalent chromium (Cr⁶⁺). The pre-treatment procedure for analysis of Cr⁶⁺ follows the standard method procedure of wastewater analysis in Japan (JIS K 0102).

RESULTS AND DISCUSSION
A number of factors should be taken into consideration in the study of elution behavior of metal alloys. The mechanism and behavior of alloys are more complex than that of pure material. Elution behavior of alloys in HTHP treatment process has accumulated from both scientific and engineering point of view. The elution behavior of metals may depend on various factors. Temperature variations and contact time play an important role. The change in temperature results into dramatic change in water properties such as; ion product, dissociation constant,
dielectric constant, solubility, etc., thus, affecting elution process. The material components of reactors having different reactivity, affinities and resistance ability at elevated temperature affect metal elution process as well.

**Effect of Temperature on Metal Elution**

From the results of the study on the effect of temperature on the amount of metal elution, it was observed that the highest eluted metal was obtained around sub-critical conditions. This observation agrees with previous findings on corrosion behavior (Kritzer *et al*., 1998 and Latanision *et al*., 1997) and could be explained by the high ion product at that condition. At sub-critical conditions, compare to supercritical conditions, the ion product of water increase significantly. Large amount of dissociated ions and high dielectric constant might promote elution. Figure 1 illustrates the effect of temperature on the amount of metal elution from SUS 316 and Inconel 625 at a contact time of 30 s (defined as mg/l-cm² of contact area). The amount of eluted metals did not coincide with metal composition of reactor materials (SUS 316 consist of 65%Fe, 18%Cr, 12%Ni, 2%Mo, 1%Mn, and Inconel 625 consist of 60%Ni, 20%Cr, 9%Mo, 5%Fe).

![Figure 1. Effect of temperature on the amount of metal elution from SUS 316 and Inconel 625 (contact time = 30 s)](image)

In some cases, iron (for SUS 316) and nickel (for Inconel 625) are not dominant. It was observed that Fe from SUS 316 is dominant at 400°C and after 90s, and Ni from Inconel is dominant around 300-400°C and at almost tested contact time. Cr, which is responsible for the formation of oxide protective layers, is not the major eluted metal in all conditions. At 300°C, Cr is unstable, resulting in selective dissolution of Cr. In case of SUS 316, at 250°C, Cr was below the detection limit of ICP as seen in Figure 1. However, at 300°C and contact time of 30s, eluted Cr increases significantly, then decreases dramatically at 400°C. The elution of Mo from SUS 316 does not follow a regular trend, the highest eluted amount was observed at 350°C. Other elements—namely Ni, Fe, and Mn, are more protective even at subcritical conditions.

Similar behavior was observed from Inconel 625 consisting of 20%Cr. However, only small amount of Cr can be detected (by ICP) at 250 and 400°C. At temperature range of 250 to 400°C at residence time of 30 s, amount of eluted metals from SUS 316 is higher than Inconel 625.

**Effect of Contact Time on Metal Elution**

**Eluted metal from Inconel 625**

The amount of eluted metal for Inconel 625 was dependent on residence time. Total eluted metal increase with increasing time, nevertheless amount of eluted elements showed the erratic behavior. The time–dependent behavior of each eluted metal will be discussed in this section. Figure 2 shows that the amount of Cr decreases with increasing time suggesting the stability of Cr increases gradually, presumably due to the complete formation of oxide protective layer. It was observed that at temperature range of 250 to 400°C, and residence time of 30 to 600s, eluted Cr from Inconel 625 decreases with increasing time. This indicates that a passive layers gradually forms as the alloy is exposed to HTHP conditions. At supercritical conditions, only small amount of Cr was eluted and the amount was stable when the residence time was increased.

![Figure 2. Effect of contact time on the amount of metal elution from Inconel 625 (T = 300°C)](image)

Nickel, from which Inconel 625 is mostly made of, was found in all tested conditions. At 300°C, from 30 to 90s, the amount of Ni increases with increasing time, then becomes stable after 240s. At 600s, the amount of eluted Ni is 0.5 ppb/cm². Under hydrothermal conditions, it is likely that Ni might also react with Cr, promoting formation of protective layers as demonstrated in reactions 1-3:

\[
2(Cr^{3+})_{alloy} + 3H^+ + 3OH^- \rightarrow Cr_2O_3 + 3H_2 \quad (1)
\]

\[
(Ni^{2+})_{alloy} + H^+ + OH^- \rightarrow NiO + H_2 \quad (2)
\]

\[
NiO + Cr_2O_3 \rightarrow NiCr_2O_4 \quad (3)
\]

Under sub–critical conditions investigated in this work, eluted Mo increases with increasing time resulting to selective dissolution of Mo. At 300°C, as illustrated in Figure 2, it was observed that the amount of Mo increases 4 times with the increase of about 10 times in the residence time. At supercritical conditions,
eluted Mo is stable after 120s. The presence of Mo in Ni-based alloys substantially improves resistance to non oxidizing acids, and when used at elevated temperatures, will lower corrosion resistance of nickel-based alloy (Craig and Anderson, 1995). At 300°C, Fe, the minor element of Inconel 625 was clearly detected by ICP. At this condition, eluted Fe was observed after 90s showing better resistance stability at short contact time. Eluted Fe then decreases at 600s.

Eluted metal from SUS 316
As can be seen in Figure 1, at temperature of 250°C, the amount of Cr eluted from SUS 316 was below detection limit of ICP. Cr is dominant at 300 and 350°C. Figure 3 shows that the stability of Cr decreases with increasing time. At 300°C, selective dissolution of Cr was observed from 6-240s. Then it becomes stable after 240s resulting to the decreasing in elution. This results seem to be different with elution from Inconel 625, probably due to the stability of reactor material under elevated conditions are different. The same trend was also observed at 350°C. Moreover, at 400°C, Cr is below detection limit of ICP. Mo, the minor element in this material decreased with increasing time at 250 and 400°C. The highest amount of Mo was observed at 300°C, and increased with increasing time.

Even only small amount of Ni, Mn and Fe eluted based on the results in Figure 3, the trend shows that the amount of Ni decrease with increasing time at 300°C. The stability of Ni was observed at subcritical conditions. However, at supercritical condition eluted Ni is almost stable during the tested time.

Another minor element, Mn, was stable at 250°C. The elution amount of Mn increased with increasing time at 300 and 350°C, and decreases with increasing time at supercritical condition. Minor elements may also affect the properties of the chromia scale (Kofstad, 1998). Mn, for instance, has proven to be beneficial in that MnO combines with Cr₂O₃ to form protective layers of MnCr₂O₄.

Fe, the major element of SUS 316, decreases with increasing time at 250 and 350°C. However, at 300 and 400°C, eluted Fe increases with increasing time.

As previously discussed, the elution phenomena of both Inconel 625 and SUS 316 different either with time or temperature. The summary for time-dependent behavior of elution for both reactors is shown in Table 1.

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. The results are illustrated in Figure 4. At subcritical conditions (250-350°C), the amount of eluted metal from SUS 316 was higher in the presence of air. The presence of oxygen slightly alters the metal elution, presumably due to the acceleration of anodic oxidation process. However, surprisingly, after supercritical condition, the absence of air promotes elution. It was observed, as well, that at 400°C, the presence of air favors elution of Mo. However the absence of air is favorable to elution of Fe. One possibility is, the absence of air will enrich the concentration of H⁺ and lowering the stability of Fe. Vice versa on elution of Mo in enrichment of OH⁻ concentration. Nevertheless, the presence or the absence of air does not affect the amount of Mo elution.

| Materials and Conditions | Mo | Cr | Ni | Fe | Mn |
|-------------------------|----|----|----|----|----|
| SUS 316                 |    |    |    |    |    |
| 250°C                   | -- | ND | -- | -- | ±  |
| 300°C                   | ++ | ++ | -- | ++ | ++ |
| 350°C                   | ++ | -- | after 240s | -- | ++ |
| 400°C                   | -- | ND | ±  | ++ | -- |

| Inconel 625             |    |    |    |    |    |
| 250°C                   | ++ | -- | after 240s | -- | ++ |
| 300°C                   | ++ | ND | after 120s | ±after 240s | -- | after 240s |
| 350°C                   | ++ | -- | ±after 120s | ND |
| 400°C                   | ±after 120s | -- | ++ | ND |

++ : Increased with increasing time  ND : Below detection limit of ICP
-- : Decreased with increasing time  ± : Stable

Figure 3. Effect of contact time on the amount of metal elution from SUS 316 (T = 300°C).
Metal Elution in Cysteic Acid Solution

Additional experiments on the effect of solution other than water on metal elution were also performed at subcritical conditions in a batch reactor made of SUS 316 and Inconel 625. The results from the Figure 5 show that in cysteic acid solution and at subcritical conditions, Fe is favorable even for Inconel 625 which is Ni-based alloy.

In agreement with previous finding on corrosion (Mitton et al., 2000), selective dissolution of Ni is observed in Ni-based alloys, while Cr is stable. In both materials Cr was detected at around 240-280°C, then decreased when temperature reach 300°C. In contrast, the corrosion product in Natrium chloride solution at subcritical conditions are enriched in Cr and depleted in Ni and Fe (Kritzer et al., 2000). Figure 6 shows the effect of contact time on the amount of metal elution from SUS 316 and Inconel 625 at 280°C. In both materials, the amount of eluted Fe is significantly increased at 4-6 min, then decreased when reaction time reach 8 min. Small amount of Ni, Mn and Mo were detected in SUS 316, while significant of Ni was observed in Inconel 625.

Elution Mechanism

Since the behavior of metals and water change under HTHP conditions, the reason for the erratic behavior of elution of metal alloys under HTHP conditions has not been clearly understood. Figure 7 describes schematically the speculated mechanism of elution of metals under HTHP conditions. The elution process is might accelerated by the relative motion of water (media) and the metal surface. Elution observed even at short contact time suggests that time progresses and increasing in temperature initiate the elution. Starting from the clean surface, the elution process might involve absorption of OH⁻ into metal surface to form metal hydroxides. The formation of metal oxides from metal hydroxides depends on temperature. For instance, the transformation of Ni(OH)₂ to NiO is at about 200-285°C (Zieminak et al., 1989). Elution would result into either formation of metal hydroxides or metal oxides.

Figure 4. Effect of the presence of air on the amount of metal elution at various temperatures (SUS 316, residence time = 30s).

Figure 5. Effect of temperature on the amount of metal elution from various materials (contact time = 2 min, Media: Cysteic acid).

Figure 6. Effect of contact time on the amount of metal elution from various reactor materials at 280°C (Media: Cysteic acid).

It can be seen that the elution from Inconel 625 follows the trend of SUS 316. However, total eluted metals from SUS 316 were much higher than Inconel 625.

Results of this experiment show that the amount of elution increased very significant under acidic compare to that of neutral conditions (when water is used as a media). Moreover, the dominant element was also different. For example, in water, Cr is favorable in SUS 316, while Fe becomes dominant when acid media is used.
Role of Chromium

From the standpoint of resistance ability at elevated temperature process, the most important alloying element is Cr. The presence of Cr which is responsible for the formation of protective layers become interesting since the amount of eluted Cr varies with both time and temperature. Carranza and Alvarez (1995) have studied the effect of temperature on the formation of passive film on alloy 800 in aqueous and sulphate solutions at temperature ranging from 60 to 280°C (by means of AC impedance measurement). The presence of soluble metal observed in this experiment suggests that the oxide layer is non-protective. In both solutions, the passive film was found to become more porous, and hence less protective with increasing temperature. The results seem to coincide with the present observation. However, these researches results show that the amount of eluted Cr decreases at 400°C which indicates that the passive film become more protective under supercritical conditions. Still, only limited information are available on the influences of other variables, such as temperature, on the properties of protective oxide film. Amount of Cr consists in alloy might take account on inhibits elution process. Agree with previous research (Mitton et al., 2000), it was observed that, in HTHP process, Inconel 625 (20% Cr) is more protective than SUS 316 (18% Cr).

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 HTHP process for wastewater treatment, the presence of trace amounts of metals has no significant effect as long as these concentrations 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 (1993) detected traces of Cr VI in the effluent of hydrothermal treatment of sludge at 400°C. Kofstad (1988) also reported the formation of Cr VI in high oxygen activities by the reaction:

\[ \text{Cr}_2\text{O}_3 + 2\text{O}_2^{2-} + 3/2\text{O}_2 \Leftrightarrow 2\text{CrO}_4^{2-} \]  

(4)

Another possibility is by formation dichromate:

\[ \text{Cr}_2\text{O}_3 + 2\text{O}_2^{2-} \Leftrightarrow 2\text{CrO}_4^{2-} \]  

(5)

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 (1996). The eluted Cr from Inconel 625 did not exceed the acceptable level. The amount of Cr VI from both materials is below the detection limit of ICP.

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 materials were below the level. However, under acidic conditions, when cysteic acid is used, most of eluted metals were over the standard level. Table 2 shows the comparison of eluted metals to the standard level for drinking water based on WHO guideline. Large amount of dissociated ion might promote the elution.

Results of this study imply that special attention should be pressed on the materials used in HTHP technique. Since subcritical conditions are often used in the process for recycling technology and resources recovery, the selected materials should withstand to the harsh conditions in order to eliminate heavy metals contamination in the product. While feed modification such as introduce base to neutralize the conditions (to minimize elution) might affect the product, design of high temperature materials is highly necessary. Optional reactor design such as the use of adiabatic expansion reactor (Kritzer, 1999) might be possible.

Conclusions

Under HTHP water conditions, it has been observed that elution occurred even in a short contact time. The results confirm that the highest eluted metal is not at supercritical condition, but at subcritical condition where the ion product goes a maximum. Under HTHP process, Ni-based alloy (Inconel 625) is more protective than Fe-based alloy (SUS 316). Depending on the exposure conditions, a moderate increase in reaction time results in a significant change in the elution behavior of these alloys. At 300°C, as time progresses, the soluble metal from SUS 316 was found to be enriched in Cr and depleted in Ni, Fe Mo and Mn. Conversely, within the same temperature, the enrichment of Ni and depletion of Cr was observed from Inconel 625. Temperature, time and materials are contributory factors in elution phenomenon.

| Metals | Reaction media: Water | Reaction media: Cysteic acid |
|--------|----------------------|-----------------------------|
|        | SUS 316 | Inconel 625 | SUS 316 | Inconel 625 | SUS 316 | Inconel 625 |
| Fe     | BSL     | BSL         | OSL     | OSL (except 200°C) |
| Mn     | BSL     | -           | BSL (except 260°C, 8-10 min) | OSL |
| Cr     | OSL     | BSL         | OSL     | OSL |
| Mo     | OSL at 350°C | BSL         | OSL at 240-300°C | OSL (except 240, 220°C and 2 min) |
| Ni     | BSL     | OSL at 300°C | OSL     | OSL |

BSL: Below the standard level
OSL: Over the standard level

Table 2. Results of the amount of eluted metals as compared to the WHO environmental quality standard for drinking water
The presence of air under subcritical conditions promotes elution. Surprisingly, at supercritical conditions, elution decreased. The results from this study has alleviated doubt regarding the elution of heavy metals under HTHP process and might contributes for development of this technique prior to building full scale operational plant.

In the environmental and health impact point of view, in some cases, the amount of eluted metals could be over the standard water quality level, depending on the operation conditions, material construction and reaction media.

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