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# Process Development for Recovery of Vanadium and Nickel from Heavy Oil Fly Ash by Leaching and Ion Exchange

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## ABSTRACT

A process for recovering V and Ni from oil fly ash and for making the ash harmless has been developed. More than 80% of V and Ni are recovered. This process involves two-step leaching and ion exchange. The first step is leaching with water to dissolve Ni, Mg, Al, and Zn, and acid solution is used in the second step to recover V. The metals Ni and V are separated from other metals in each leached liquor. After neutralization and oxidation of the first liquor, Fe and Al are precipitated and removed from solution. Both Ni and Zn are then loaded on CR20 resin. Nickel can be selectively desorbed from the resin due to a remarkable difference in ion exchange isotherm between Ni and Zn. By using the resin C467, V is selectively separated from the second leached liquor containing V and Fe.

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The advantage of this separation process is that acidic leachant can be reused, saving separation energy.

*Key Words:* Fly ash; Leaching; Ion exchange; Vanadium; Nickel.

## INTRODUCTION

A large amount of fly ash is generated in power plants, most of which is disposed as industrial waste. The ash mainly consists of porous unburned carbon, metal oxides, and water-soluble sulfates. The dissolution of sulfates with metals results in the release of harmful heavy metal ions to the environment. Metals contained in fly ash derived from heavy oil include vanadium and nickel, together with iron and aluminum. The V content in oil fly ash is 1–7%, and this is comparable to that found in its mineral resources.[1] Recently, the reuse of waste ash has been attracting notice from the viewpoint of environmental protection and resource conservation. Several processes to recover valuable metals such as V or Ni from oil or coal fly ash have been proposed.[1–4] However most of them have a high impact on the environment. Extraction or precipitation of metals and neutralization of wastewater require costly reagents, which may cause additional pollution. In this regard, the ion exchange process are advantageous. Target ions are removed without adding chemicals in ion exchange techniques. A closed water system is easily attained by leachant recycling, and thus additional facilities for wastewater treatment are eliminated. A number of studies have applied ion exchange resins for the removal and the recycling of heavy metal ions from various wastewaters of metal plating, alloy industries, pigments, etc.[5–9]

In this work, a process has been developed to recover V and Ni selectively and to make the fly ash less harmful. This process includes two-step leaching followed by ion exchange of the leached liquor. Leaching was carried out by using water, HCl, $H_2SO_4$, and NaOH as leachant. Ion exchange equilibria were also investigated for the recovery of nickel and vanadium.

## EXPERIMENTAL

### Ash Sample

Oil fly ash used was obtained from an electrostatic precipitator of a power plant located at Kimizu, Japan. Fuel for the plant was a mixture of high sulfur content C grade heavy oil (40%) and coke-oven gas (60%). Ammonia was added into the flue gas stream to neutralize the sulfuric acid generated from the fuel burning.

In this study, target metals in the ash were V, Ni, Fe, Al, Mg, and Zn. The selection of the target metals was based on the fluorescent x-ray analysis of the fly ash. Target metal concentrations in the ash were determined quantitatively by digesting the dried ash in a hot mixed acid composed of concentrated $HClO_4$, $H_2SO_4$, and $HNO_3$ and ICP-AES analysis.

## Leaching

Leaching was carried out by mixing 2 g dried ash with 50 $cm^3$ leachant in a glass flask for 6 hr at 298K. After filtration with qualitative-grade filter paper, metal concentrations in the leached liquor were measured with ICP-AES; the fraction of metal leached out was defined as the metal amount leached out divided by that contained in 2 g dried ash, where the amount leached out equals the metal concentration multiplied by total volume of leachant, 50 $cm^3$. Deionized water, acid solutions (HCl and $H_2SO_4$), and alkaline solution (NaOH) were tested as leachants. Concentrations of each acid or alkaline solution were 1, 0.1, 0.01, and 0.001 $kmol/m^3$.

## Recovery of Metals from Leached Liquors by Ion Exchange

Ion exchange resins used in this study are commercial strong acid type, DIAION SK1B, and chelating types, DIAION CR11, DIAION CR20, and DUOLITE C467 (DIAION: Mitsubishi Chemical Co.; DUOLITE: Rohm and Haas). Their characteristics are listed in Table 1. SK1B, CR11, and C467 are available in Na-form. Prior to the measurement, the resins were converted to H-form with 1 $kmol/m^3$ HCl solution. Metal solutions were prepared by dissolving respective metal sulfates in $H_2SO_4$ or metal chlorides in HCl.

Ion exchange equilibrium was measured by a batch method. The solution was equilibrated with the resin in a test tube by shaking at 298K for 3 hr (SK1B) or 2 days (CR11, CR20, and C467). The reason why 2 days is taken is to ensure reaching equilibrium. This was not because of the slow reaction. The equilibrium concentrations of metals in the liquid phase were measured by ICP-AES. Metal concentration in the resin phase, $q$, was calculated by the mass balance.

$$q = \frac{(C_0 - C)L}{V} \tag{1}$$

***Table 1.*** Characteristics of ion exchange resins.

| Resin | DIAION SK1B | DIAION CR11 | DIAION CR20 | DUOLITE C467 |
|---|---|---|---|---|
| Polymer matrix | Gel styrene–DVB | Macroporous styrene–DVB | Macroporous styrene–DVB | Macroporous styrene–DVB |
| Functional group | $—SO_3^{\ -}$ | $—CH_2N(CH_2COO)_2^{\ 2-}$ | $—CH_2NH—(CH_2CH_2NH)_nH$ | $—CH_2NHCH_2PO_3^{\ 2-}$ |
| Density, kg/m$^3$ | 1276 | 1130 | 1055 | 1120 |
| Moisture retention[a] % | 43–50 | 55–65 | 50–60 | 60–65 |
| Saturation capacity[a] keq/m$^3$ | Above 2.0 | Above 1.0 (for $Cu^{2+}$) | Above 0.8 (for $Cu^{2+}$) | — |

[a] Data based on the supplied technical catalog.

where $C_0$ and $C$ are initial and equilibrium concentrations in liquid phase, respectively. $L$ and $V$ are volume of the solution and the resin, respectively. In this experiment, $L$ was 20 $cm^3$ and $V$ was varied.

## RESULTS AND DISCUSSION

### Leaching Behavior of Ash in Acid or Base Solution

Target metal concentrations in the fly ash are listed in Table 2. Values are averaged for three runs. It is noteworthy that Fe content is the largest and the separation of V and Ni from Fe is crucial in the present situation.

Effect of acid concentration on the leached fraction of metals for dilute $H_2SO_4$ solution is shown in Fig. 1. Fractions of Mg, Ni, Al, and Zn are relatively high for all acid concentrations. The fractions of Fe and V increase with acid concentration, and the slope for V is steeper than that for Fe. Leaching fraction of metals with various leachants as well as metal concentration in leached solution are summarized in Table 3. No remarkable difference in leaching is found between HCl solution and $H_2SO_4$ solution. When NaOH solution is used, the fraction of V increases with increasing leachant concentration in a similar manner as acid leaching, but the fraction is somewhat lower. On the other hand, Fe, Mg, and Ni are not leached out even at high concentration of NaOH. With increasing NaOH concentration, leaching fraction of Al and Zn drops down to the minimum at 0.1 $kmol/m^3$ NaOH and increases after. This is attributable to the formation of hydroxides and anion complexes with increasing pH value.

Although the selective leaching of V is possible with concentrated NaOH solution, other metals remaining in the residual ash will cause a problem if it is landfilled. Thus, these metals should also be removed with acids in excess over the added NaOH, with the result of energy loss for neutralization. By the use of very dilute acid and water, large amounts of metals except for V and Fe were leached out. The pH value of the solution obtained by leaching with water was 2.70, which was approximately the same as the one by the leaching with dilute acidic solutions. The low value of pH is due to the dissolution of sulfate contained in the original ash. Such dissolution results in the release of heavy metal ions. On the other hand, V dissolves in aqueous solutions at pH values lower than 2. Taking account of these facts, we propose a two-step leaching: the first step is leaching with water for removal of Ni, Mg, Al, and Zn, and the second step is leaching with acid solution for recovery of V.

***Table 2.*** Metal contents (wt%) of the fly ash determined by ICP-AES after acid digestion.

| V | Ni | Fe | Mg | Al | Zn |
|---|---|---|---|---|---|
| 0.767 | 1.80 | 5.98 | 0.343 | 0.287 | 0.111 |

For the case of leaching with water, the leaching fraction of metals was independent of leaching time in the present experimental conditions (1–6 hr). Effect of liquid/solid ratio (L/S) on the extent of leaching is shown in Fig. 2. The amount of the fly ash was varied against 50 $cm^3$ of water. Leaching fractions of Mg, Ni, Al, and Zn are relatively high and are independent of L/S ratio. Such a constant fraction suggests that the liquid amount is large enough to dissolve all soluble metals even at $L/S = 2.5$. Vanadium is scarcely leached out with water, and its leaching fraction slightly decreases with the increase in L/S due to the increase in pH. In view of metal recovery, concentrated solutions are suitable. However in the operation at low L/S ratio (e.g., at 2.5), the amount of liquid separated from solid reduced largely because the ash retained a large

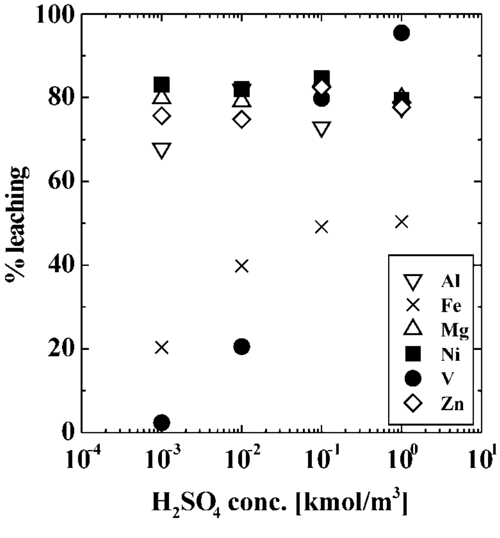

***Figure 1.*** Effect of $H_2SO_4$ concentration on leaching of metals from fly ash.

*Table 3.* Leached fraction of metals with various leachants.

| Leachant | | V | Fe | Mg | Ni | Al | Zn | pH | Color |
|---|---|---|---|---|---|---|---|---|---|
| Water | ppm | 8.3 | 380 | 105 | 620 | 84.1 | 36.5 | 2.70 | Yellow |
| | % leaching | 2.7 | 15.6 | 75.2 | 84.7 | 71.9 | 81.0 | | |
| HCl (1 kmol/m$^3$) | ppm | 291 | 1184 | 117 | 580 | 92.5 | 34.5 | 0.16 | Green |
| | % leaching | 94.2 | 49.1 | 84.5 | 80.1 | 79.8 | 77.4 | | |
| HCl (0.1 kmol/m$^3$) | ppm | 270 | 1240 | 103 | 613 | 93.1 | 33.9 | 0.51 | Green |
| | % leaching | 87.3 | 51.3 | 74.7 | 84.5 | 80.2 | 75.9 | | |
| HCl (0.01 kmol/m$^3$) | ppm | 18.3 | 791 | 104 | 627 | 86.6 | 37.3 | 2.54 | Yellow |
| | % leaching | 5.9 | 32.8 | 75.2 | 86.7 | 74.8 | 83.7 | | |
| HCl (0.001 kmol/m$^3$) | ppm | 14.1 | 426 | 98.9 | 594 | 84.1 | 35.8 | 2.60 | Yellow |
| | % leaching | 4.6 | 17.8 | 72.2 | 82.6 | 73.2 | 80.9 | | |
| $H_2SO_4$ (1 kmol/m$^3$) | ppm | 294 | 1210 | 110 | 574 | 89.7 | 34.6 | 0.19 | Blue |
| | % leaching | 95.5 | 50.4 | 79.9 | 79.5 | 77.7 | 77.7 | | |
| $H_2SO_4$ (0.1 kmol/m$^3$) | ppm | 249 | 1200 | 117 | 620 | 85.4 | 37.2 | 1.13 | Green |
| | % leaching | 79.8 | 49.1 | 83.9 | 84.7 | 73.0 | 82.4 | | |
| $H_2SO_4$ (0.01 kmol/m$^3$) | ppm | 63.6 | 963 | 110 | 596 | 95.1 | 33.5 | 2.40 | Yellow |
| | % leaching | 20.6 | 39.8 | 79.0 | 82.0 | 81.9 | 74.8 | | |
| $H_2SO_4$ (0.001 kmol/m$^3$) | ppm | 7.4 | 493 | 111 | 605 | 79.0 | 33.9 | 2.66 | Yellow |
| | % leaching | 2.4 | 20.4 | 79.8 | 83.1 | 67.8 | 75.7 | | |
| NaOH (1 kmol/m$^3$) | ppm | 208 | 0.7 | 0.0 | 1.3 | 58.6 | 4.4 | 13.96 | Colorless |
| | % leaching | 67.4 | 0.03 | 0.0 | 0.18 | 50.5 | 9.86 | | |
| NaOH (0.1 kmol/m$^3$) | ppm | 60.2 | 0.2 | 0.2 | 0.6 | 11.9 | 0.0 | 11.83 | Colorless |
| | % leaching | 19.7 | 0.1 | 0.2 | 0.1 | 10.3 | 0.0 | | |
| NaOH (0.01 kmol/m$^3$) | ppm | 6.2 | 115 | 111 | 582 | 77.0 | 33.9 | 2.85 | Green |
| | % leaching | 2.0 | 4.78 | 80.3 | 80.4 | 66.6 | 76.2 | | |
| NaOH (0.001 kmol/m$^3$) | ppm | 10.9 | 334 | 109 | 602 | 78.6 | 33.9 | 2.66 | Yellow |
| | % leaching | 3.5 | 13.9 | 78.8 | 83.1 | 67.8 | 76.0 | | |

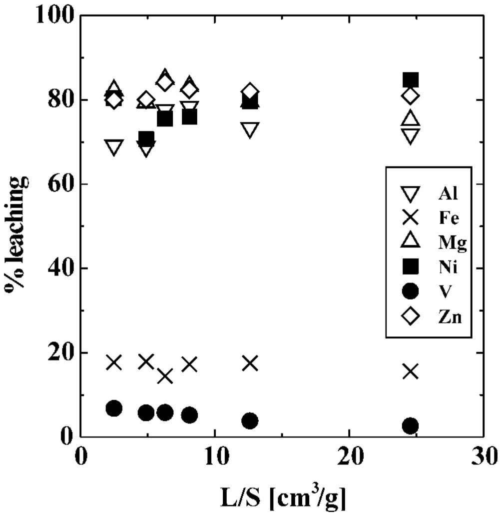

*Figure 2.* Effect of ratio of leachant volume to amount of ash (L/S) on extent of metal leaching of metals from fly ash.

portion of liquid. Therefore, the L/S ratio over five is practically preferable in batch leaching.

## Recovery of Nickel

The solution after water leaching contains Ni and Fe at relatively high concentration as well as Mg, Al, and Zn (Table 3). A large fraction of Fe along with Al is precipitated and filtered out from the solution through the pH control using NaOH before recovering nickel by the ion exchange. Figure 3 shows the fractions of metals remaining in solution after removing the precipitate, which are determined from concentration ratio after and before the treatment. About 80% of Fe is removed under the condition of $pH > 3$ and almost all of Al precipitates at $pH = 5$. Remaining Fe ion in the solution must be the divalent ion Fe(II) because the solubility of Fe(II) is much greater than that of Fe(III) at this pH. Therefore, if the Fe(II) ion was wholly oxidized to Fe(III), Fe ion would be deeply separated from the solution. This was confirmed by adding hydrogen peroxide to the Fe(II) solution. Ions of Ni, Mg, and Zn still remain in solution after the pH controlled precipitation. Recovery of Ni from the solution was conducted by ion exchange with CR20 resin.

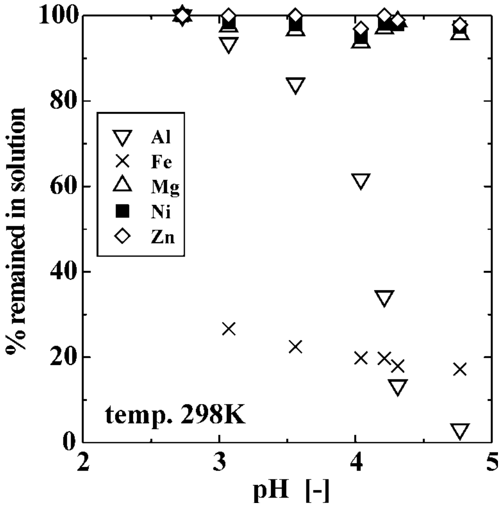

***Figure 3.*** Remaining fraction of metals in filtrate after pH adjustment of the solution obtained from water leaching.

Performance of this resin can be seen in Fig. 4, which is the ion exchange equilibrium of CR20 resin with the solution of Ni or Zn. Magnesium was not loaded on CR20. Nickel and Zn were removed from the solution by ion exchange with CR20, and the resultant solution contained only Mg. The value of pH after ion exchange was approximately 7. This is most likely due to the attraction of $H^+$ ion to functional group of CR20 resin, which is polyamine. When Ni and Zn are desorbed from CR20 by acidic solution, these ions can be mutually separated by controlling pH according to the difference in their affinity for the resin.

## Recovery of Vanadium

Following the first leaching with water, the second leaching by acid solution was performed, and V and Fe were leached out. To separate V from Fe in the leached liquor, ion exchange was applied. Resin listed in Table 1 was tested. All measurements were carried out in the range of pH 1.04–1.10, and the ion exchange was conducted from the single system. Separation capability of the resins is evaluated from ion exchange equilibrium, and the ion exchange equilibria for SK1B and C467 are shown in Figs. 5 and 6, respectively. SK1B

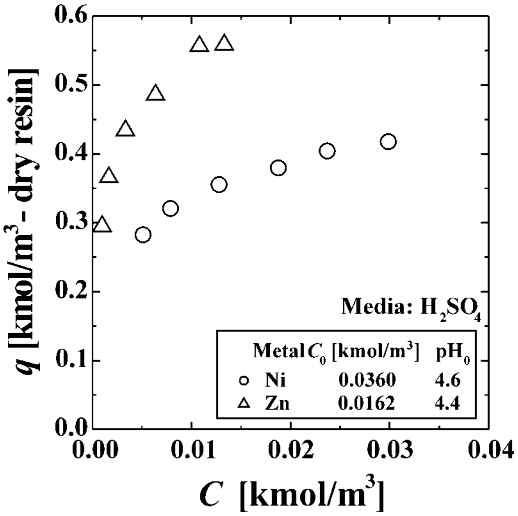

***Figure 4.*** Equilibria for ion exchange of Ni and Zn on CR20 resin.

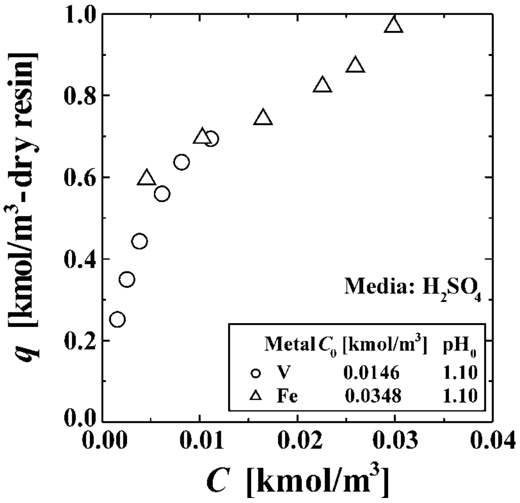

***Figure 5.*** Equilibria for ion exchange of V and Fe on SK1B resin.

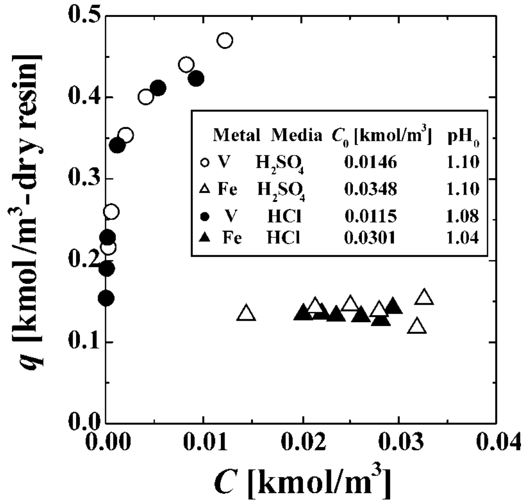

***Figure 6.*** Equilibria for ion exchange of V and Fe on C467 resin.

resin loads large amounts of V and Fe as shown in Fig. 5, which shows no difference in the selectivity between the two metals. Among the examined resins, C467 resin loads V selectively and a marked difference is found in amounts of V and Fe loaded, where the ion exchange behavior in HCl and $H_2SO_4$ media is quite similar. Although data are not shown here, ion exchange of V on C467 resin from binary mixture of V and Fe has been examined. The trends of metal concentration in resin phase, $q$, were similar to those for single metal system. The metal-ion loading was apparently small because of cofixation of V and Fe on the resin. Separation factor of V, $(q_V/C_V)/(q_{Fe}/C_{Fe})$, in the binary mixture was about three and was unaffected by the pH value (0.42–1.43). This value of separation factor is similar to the ratio of loaded amounts of V and Fe in the single system.

## Process to Recover Vanadium and Nickel

Our proposal for the process to recover metals from fly ash is shown in the form of flowsheet in Fig. 7. The most important point is that it is a two-step leaching process. Most Ni, Mg, Al, and Zn in the fly ash are removed in the first leaching step with water. If Ni, Mg, Al, and Zn remain in the fly ash after the first step, repeated leaching with water is recommended, which leads to

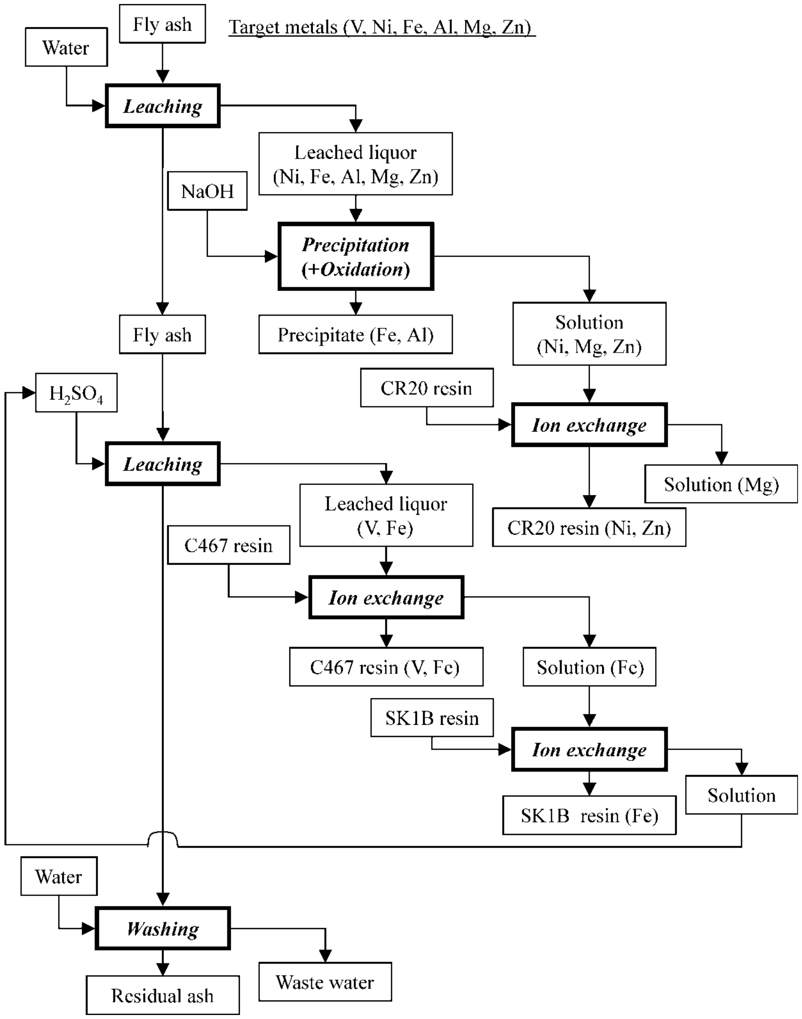

*Figure 7.* Flowsheet of process for recovering metals from oil fly ash.

a high degree of leaching for these four metals and eases the following step to recover V.

A large fraction of Fe and Al are precipitated by the pH adjustment with NaOH (to pH = 5) and removed from the leached liquor. Nickel and Zn are recovered by CR20 resin from the solution after precipitation separating them

***Table 4.*** Result of recovering metals from 10 g fly ash by the process developed in this study.

| Step (condition) | | V | Fe | Mg | Ni | Al | Zn | $V_{sol}$ [cm$^3$] | pH |
|---|---|---|---|---|---|---|---|---|---|
| 1st water leaching (100 cm$^3$) | mg | 1.27 | 51.5 | 13.1 | 73.2 | 8.18 | 4.62 | 80 | 2.71 |
| | %[a] | 2.8 | 21.0 | 68.1 | 75.0 | 50.0 | 73.0 | — | — |
| In precipitate | mg | 1.27 | 51.5 | 0 | 0 | 8.18 | 0 | — | — |
| | % | 2.8 | 21.0 | 0 | 0 | 50.0 | 0 | — | — |
| In solution after ion exchange (CR20 11.4 cm$^3$) | mg | 0 | 0 | 10.5 | 3.53 | 0 | 0.04 | 88 | 4.79 |
| | % | 0 | 0 | 68.1 | 4.5 | 0 | 1.1 | — | — |
| In CR20 resin | mg | 0 | 0 | 0 | 53.7 | 0 | 2.56 | — | — |
| | % | 0 | 0 | 0 | 70.5 | 0 | 71.9 | — | — |
| 2nd water leaching (100 cm$^3$) | mg | 0.74 | 4.73 | 2.30 | 13.2 | 1.87 | 0.88 | 70 | 2.80 |
| | % | 1.6 | 1.9 | 12.0 | 13.5 | 11.5 | 13.9 | — | — |
| In precipitate | mg | 0.74 | 4.73 | 0 | 0 | 1.87 | 0 | — | — |
| | % | 1.6 | 1.9 | 0 | 0 | 11.5 | 0 | — | — |
| In solution after ion exchange (CR20 5.4 cm$^3$) | mg | 0 | 0 | 2.30 | 1.90 | 0 | 0.05 | 68 | 4.70 |
| | % | 0 | 0 | 12.0 | 2.1 | 0 | 0.9 | — | — |
| In CR20 resin | mg | 0 | 0 | 0 | 9.10 | 0 | 0.60 | — | — |
| | % | 0 | 0 | 0 | 11.4 | 0 | 13.0 | — | — |

(*continued*)

***Table 4.*** Continued.

| Step (condition) | | V | Fe | Mg | Ni | Al | Zn | $V_{sol}$ [cm$^3$] | pH |
|---|---|---|---|---|---|---|---|---|---|
| 1 kmol/m$^3$ $H_2SO_4$ leaching (150 cm$^3$) | mg | 33.9 | 101 | 0.77 | 3.81 | 2.24 | 0.27 | 115 | 0.33 |
| | % | 75.0 | 41.2 | 4.0 | 3.9 | 13.7 | 4.3 | — | — |
| In solution after ion exchange (CR467 17.6 cm$^3$) | mg | 1.33 | 1.32 | 0.73 | 3.62 | 1.51 | 0.10 | 115 | 0.33 |
| | % | 3.0 | 0.5 | 3.8 | 3.7 | 9.3 | 1.6 | — | — |
| In C467 resin | mg | 32.6 | 100 | 0.04 | 0.19 | 0.73 | 0.17 | — | — |
| | % | 72.0 | 40.6 | 0.2 | 0.2 | 4.4 | 2.6 | — | — |
| Washing (100 cm$^3$) | mg | 4.43 | 14.3 | 0.26 | 0.65 | 0.69 | 0.06 | 82 | 0.98 |
| | % | 9.8 | 5.9 | 1.3 | 0.7 | 4.2 | 0.9 | — | — |
| In solution after ion exchange (CR467 4.6 cm$^3$) | mg | 0.03 | 0.07 | 0.22 | 0.65 | 0.01 | 0.03 | 82 | 0.98 |
| | % | 0.1 | 0.1 | 1.1 | 0.7 | 0.1 | 0.4 | — | — |
| In C467 resin | mg | 4.40 | 14.2 | 0.04 | 0.0 | 0.68 | 0.03 | — | — |
| | % | 9.7 | 5.8 | 0.2 | 0.0 | 4.1 | 0.5 | — | — |
| Residual ash | mg | 4.86 | 73.5 | 2.81 | 6.73 | 3.38 | 0.50 | — | — |
| | % | 10.8 | 30.0 | 14.6 | 6.9 | 20.7 | 7.9 | — | — |

[a] Percentage indicates the weight content in the solution, precipitate, or resin for each metal.

from Mg. That is retained in solution. The amount of Ni loaded on CR20 is larger than that of Zn because of the much higher concentration of Ni in the original solution. Nickel can be further purified by selective desorption or solvent extraction.

The water-leaching process (step one) is followed by $H_2SO_4$ leaching for the recovery of V as the second step. Vanadium and Fe are released in the leached liquor. Vanadium is then largely separated from Fe by ion exchange with C467 resin. After leaching, the ash is washed with water before disposal. The advantage of this separation process is that the acidic leachant can be reused (although it is necessary to remove Fe ion), which reduces the separation energy and thus reduces the environmental impact.

A series of the experiments depicted in Fig. 7 has been carried out batchwise, and the results of recovered metals are listed in Table 4. The mass and the percentage of each metal contained in the solution, precipitate, and resin have been noted, in which the values are calculated on the assumption that no loss occurs in filtering operation. Total Ni amount leached out after water leaching becomes 86.4 mg (73.2 + 13.2), which corresponds to 88.5% of the initial content. Other metals like Mg, Al, and Zn are also found in the solution after water leaching. However, Ni and Zn are selectively uptaken by CR20 resin. Remarkably, only a few percent of V are found in each solution at water leaching. Dissolution of V was successful with 1 kmol/m$^3$ $H_2SO_4$. Almost all (75.0% at acid leaching + 9.8% at washing) V is dissolved into solution. More than 80% of V is recovered on C467; however, an appreciably large amount of Fe is also uptaken by the resin. Because C467 resin selectively adsorbs V against Fe, a multistage operation will result in mutual separation such that the resin loaded with V and the solution containing Fe. The solution can be treated with SK1B resin to remove Fe and then recycled as acidic leaching solution.

## CONCLUSIONS

Leaching of metals from fly ash derived from heavy oil combustion was carried out by using water, acid solutions (HCl and $H_2SO_4$), and alkaline solution (NaOH) as leachants. Ion exchange equilibria between metals and various ion exchange resins were studied, and the following conclusions were drawn.

1. A process has been developed to achieve three goals: to recover V and Ni from the fly ash, to make fly ash harmless, and to reuse the leachant. More than 80% of V and Ni are recovered on C467 and CR20 ion exchange resins, respectively.

2. A relatively high degree of leaching is attained for Mg, Ni, Al, and Zn with water or acid solution of any concentration. For two-step leaching process, leaching with water for removal of Ni, Mg, Al, and Zn is followed by leaching with acid solution for recovery of V.
3. Recovery of Ni from the leached liquor of water-leaching process (containing Fe, Mg, Al, and Zn) is as follows: Fe and Al are precipitated out from the leached solution by the pH adjustment, and Fe(II) ion is oxidized by adding hydrogen peroxide. Then Ni and Zn are recovered from the solution by the ion exchange with CR20 resin.
4. C467 resin is appropriate to separate V from Fe in the leached liquor of acidic solution because this resin has the highest selectivity for V against Fe with a separation factor of 3 among the ion exchange resins studied.

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