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Recovery of Nickel and Vanadium from a Fly Ash of Bitumen-in-Water Emulsion by Chemical Vapor Transport

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Nickel and vanadium in a fly ash of bitumen-in-water emulsion, as a new fuel, were recovered with the yields of 67 and ~100%, respectively, by a high temperature chlorination and a subsequent chemical vapor transport along temperature gradient. To use a vapor complex former, $Al_2Cl_6(g)$, increased the yield of the nickel, and to optimize the temperature gradient reduced the contamination of magnesium in the recovered nickel.

A bitumen-in-water emulsion (ORIMULSION^{TM}) has been developed by British Petroleum Company p.l.c. and Petróleos de Venezuela S.A. in order to commercialize the extra-heavy bitumens from Venezuelan Orinoco region. The emulsion is of great significance for an alternative energy source for the future.[1] The combustion of the emulsion produces a large amount of fly ash which contains some rare metals, *i.e.* vanadium, nickel, and magnesium (the magnesium is an additive to stabilize the emulsion). At present, the vanadium in the fly ash is recovered industrially by means of a wet method.[2]

Vapor phase chlorination and extraction have been widely investigated for a dry metallurgical metal-recovering processes where rare metals were obtained as volatile chlorides.[3] However, non-volatile rare metal chlorides cannot be extracted with this method. On the other hand, a chemical vapor transport (CVT) phenomenon mediated by metal halide vapor complexes[4] renders possible to extract and separate the non-volatile chlorides at relatively low temperatures. We have reported recently that the separation[5-8] and recovery[9] of rare earths can be successfully conducted by a complete dry process using the CVT method.

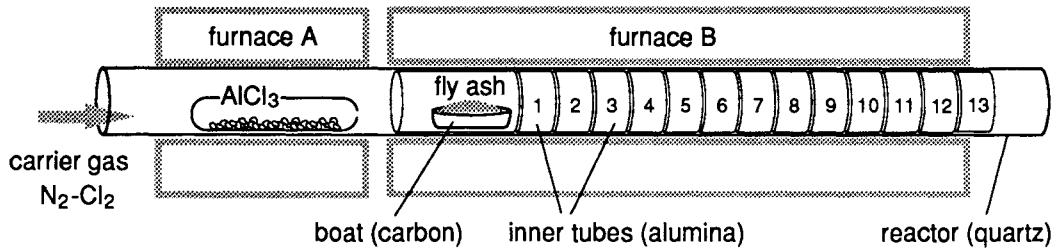

Fig. 1. Assembly of electric furnaces for the chemical vapor transport reaction. The figures, 1-13, concerning the furnace B denote the fraction numbers (*FN*).

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In the present work, the vapor phase extraction and separation characteristics of the vanadium, nickel, and magnesium from the fly ash of the bitumen-in-water emulsion were studied by the CVT method, and the resulting separation efficiency is discussed to present a flowsheet for recovering these metals from the fly ash.

The fly ash used for this work was produced during a combustion test by The Kansai Electric Power Co., Inc. The fly ash contains metal elements: V (3.5%), Ni (1.4%), Mg (7.2%), Al (1.6%), and Fe (0.73%); these metals are contained as oxides, sulfates, and other related salts. The apparatus for the CVT reaction comprises two furnaces, A and B (Fig. 1); furnace A was employed to generate the gaseous Al_2Cl_6 as a vapor complex former, and furnace B to obtain the temperature gradients for the CVT reaction. The ash was weighed (0.50 g), charged in a small carbon boat, and loaded into the reactor tube in a stream of N_2 gas (30 cm^3 min^{-1}). The complex former, $AlCl_3$ (8.0×10^{-2} mol), was sealed in a glass container with a small orifice (~0.3 mm) so as to control the evaporation rate of $AlCl_3$; the ampoule was introduced into the middle of furnace A. Furnace B was operated to heat the ash at 300-600 °C, and after the desired temperature gradient was attained, a Cl_2 gas (5 cm^3 min^{-1}) was introduced into the reactor to chlorinate the ash and, then, furnace A was heated to generate Al_2Cl_6(g). The resulting metal chloride mixture vaporized according to a simple sublimation,

$$n\,MCl_x(s) = M_nCl_{nx}(g), \quad (1)$$

or the vapor complexation with the Al_2Cl_6(g),

$$MCl_x(s) + n/2\ Al_2Cl_6(g) = MAl_nCl_{x+3n}(g), \quad (2)$$

where (s) and (g) represent solid and gas states, respectively. These vapor species were driven with the gas stream along the temperature gradient, and subsequently decomposed according to the reverse process. After the reaction lasted for 3-12 h, the resulting deposits along the temperature gradient were collected from the inner tubes. The deposits were dissolved individually in a deionized water to determine the composition of metal elements for each portion (*FN*; fraction numbers) on an X-ray fluorometry.

The vanadium was extracted thoroughly and condensed in *FN*=13 (~80 °C) without using the complex former, Al_2Cl_6(g). The chlorination of vanadium in the ash presumably gives low boiling compounds, VCl_4 (bp 149 °C) and/or VCl_3O (bp 127 °C), since other vanadium chlorides or oxychlorides are non-volatile or not stable in the temperature range of < 600 °C. Table 1 shows the yield of vanadium under several reaction conditions. The vanadium was extracted almost completely above 500 °C within 6 h. However, the

Table 1. Yield (%) of vanadium when fly ash was treated with Cl_2 gas

Reaction	Yield after reaction for			
Temperature / °C	1.5 h	3 h	6 h	12 h
600	94	~100	~100	~100
500	-	92	~100	~100
400	-	-	78	~100
300	-	-	-	12

Table 2. Yield (%) of extracted metal elements when fly ash was treated with Cl_2 and Al_2Cl_6 gases

Reaction	Reaction	Yield / %		
Temperature / °C	Time / h	V	Ni	Mg
600	12	~100	67	91
600[a)]	12	~100	27	< 0.1
600	6	~100	42	61
500	12	~100	50	79
400	12	97	< 0.1	11

a) without using Al_2Cl_6(g), complex former.

chlorination at 600 °C brought the vanadium contaminated by iron chloride ($FeCl_3$) which also deposited around *FN*=13. On the other hand, high purity vanadium chloride (or oxychloride) was obtained when chlorinated at 500 °C, since $FeCl_3$ did not evaporate in this temperature.

Though nickel and magnesium in the ash were chlorinated, the yields of these metal chlorides were low without using the $Al_2Cl_6(g)$, because the chlorides of nickel and magnesium are less volatile than vanadium chloride (or oxychloride). Only 27% and < 0.1% of $NiCl_2$ and $MgCl_2$ were extracted, respectively, when the ash was treated with Cl_2 gas at 600 °C for 12 h. In this case, however, the use of $Al_2Cl_6(g)$ improved the yield of these chlorides, since the $Al_2Cl_6(g)$ reacts with the chlorides providing the volatile complexes, $NiAl_2Cl_8(g)$[10] and $MgAl_2Cl_8(g)$.[11] The yield of nickel and magnesium increases with the increase of reaction temperature and time as summarized in Table 2. It is noteworthy that the yield of $MgCl_2$ becomes larger than that of $NiCl_2$ when the $Al_2Cl_6(g)$ is used, suggesting that the effect of vapor complexation on transport reaction is more pronounced for $MgCl_2$ than that for $NiCl_2$. This is in accordance with the Dewing's results on the volatility of divalent chlorides in the presence of $AlCl_3$,[11] where $MgAl_2Cl_8(g)$ is more volatile than $NiAl_2Cl_8(g)$ at the same temperature and the pressure of $Al_2Cl_6(g)$.

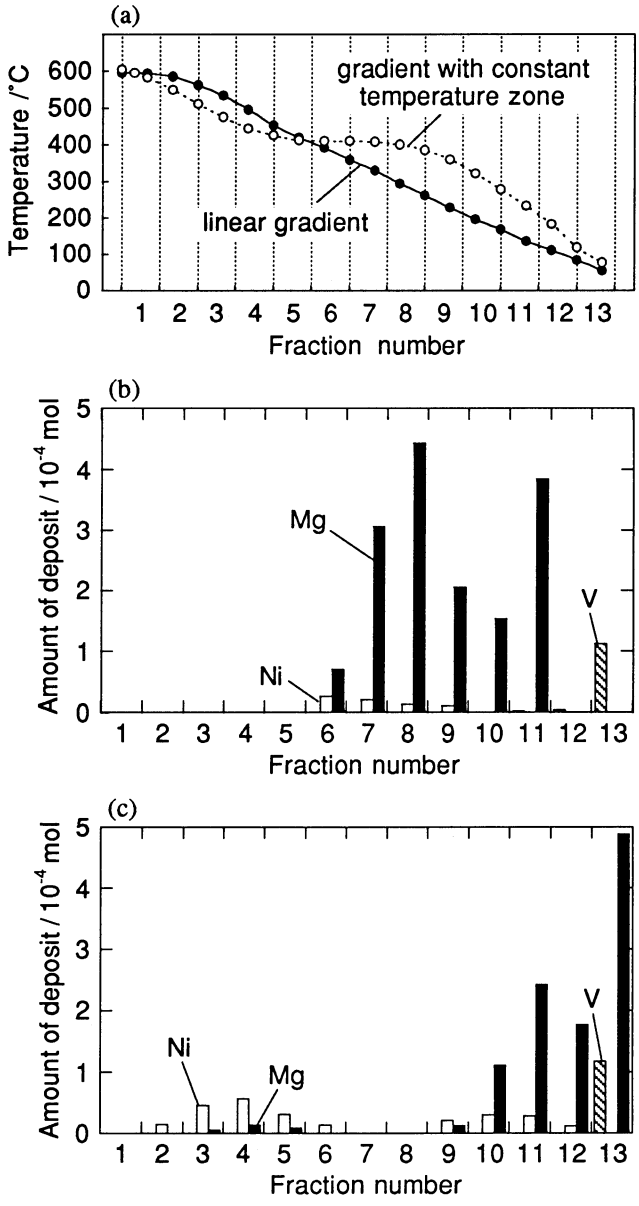

Fig. 2. Two types of temperature gradient (a), and deposition profile of nickel, magnesium, and vanadium chlorides (oxichlorides) when transported along (b) linear and (c) stepwise temperature gradients.

Figure 2 shows the deposition profile of nickel, magnesium, and vanadium chlorides together with the temperature gradient in Furnace B. When a linear temperature gradient (see Fig. 2a) was used, the deposition profile of the $NiCl_2$ (*FN*=6-9, 210-400 °C) was overlapped with that of $MgCl_2$ (*FN*=6-11, 170-400 °C). Consequently, the purity of recovered $NiCl_2$ was 6.5% even by the treatment at 600 °C for 12 h. However, a slight difference between the temperatures of two deposition maxima, *i.e.* ~400 °C for $NiCl_2$ and ~360 °C for $MgCl_2$, suggests that the mutual separation of the $NiCl_2$ and $MgCl_2$ is possible by employing a temperature gradient with a constant temperature zone around these temperatures. The deposition profile along the temperature gradient with the constant temperature zone of 410 °C (see Fig. 2a) is

shown in Fig. 2c. Under this reaction condition no deposition of the chlorides was observed around the constant temperature zone (*FN*=7, 8) and, hence, the whole deposits can be divided into two parts: Ni-rich portion (*FN*=2-6) and Mg-rich portion (*FN*=9-13). Although the yield of $NiCl_2$ was lowered (46%), the purity of $NiCl_2$ in the Ni-rich portion was nevertheless improved to 78%.

When the Al_2Cl_6(g) was used, $MgCl_2$, $FeCl_3$, and $AlCl_3$ (the complex former) also deposited at *FN*=13 and, therefore, the recovered vanadium has a low purity. Consequently, the simple chlorination by Cl_2 seems to be appropriate as for the vanadium recovery from the ash. To conclude above, the most appropriate flowsheet for recovering the vanadium, nickel, and magnesium from the Orimulsion fly ash is:

(i) chlorination of the fly ash by Cl_2 gas at 500 °C to obtain vanadium from the fraction at ~80 °C,
(ii) heating the residual mixture at 600 °C to remove the $FeCl_3$,
(iii) introduction of the Al_2Cl_6 gas to transport the $NiCl_2$ and $MgCl_2$ by the CVT reaction along the temperature gradient with the constant temperature region at 410 °C.

The reaction time of each reaction (i)-(iii) depends on the quantity of the fly ash treated.

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