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# Studies of Selective Adsorption Resins. XXII. Removal and Recovery of Arsenic Ion in Geothermal Power Waste Solution with Chelating Resin Containing Mercapto Groups

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# Studies of Selective Adsorption Resins. XXII. Removal and Recovery of Arsenic Ion in Geothermal Power Waste Solution with Chelating Resin Containing Mercapto Groups

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## Abstract

Removal and recovery of harmful arsenic ion in a geothermal power waste solution with three macroreticular chelating resins containing mercapto groups were investigated. The resin (RES), which was prepared from 2,3-epithiopropyl methacrylate-divinylbenzene copolymer beads, exhibited high affinity for arsenic(III) ion and high resistance against hot water. In the column method, arsenic(III) ion in an aqueous solution was favorably adsorbed on the RES when the sodium arsenite solution (pH 6.2) containing 3 mg/dm$^3$ of arsenic(III) ion was passed through the RES column at a space velocity of 15 h$^{-1}$. The arsenic(III) ion adsorbed was eluted by allowing 2 mol/dm$^3$ sodium hydroxide solution containing 5% of sodium hydrogen sulfide to pass through the column. The recycle of adsorption and elution was found to be satisfactory. The RES also exhibited high adsorption ability for arsenic ion in the geothermal power waste solution.

In recent years, geothermal energy has been used as one of the new energy sources for the generation of electric power. A large volume of

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high temperature waste solution (about 90°C) is produced in a geothermal power station. However, the hot water is returned underground without reuse because the waste solution contains a trace amount of harmful arsenic ion. In previous papers (*1, 2*) we reported that macroreticular chelating resins containing mercapto groups show a high affinity for arsenic(III) ion in aqueous solution. In this article the selective removal of arsenic ion from the waste solution of a geothermal power station is investigated as an application of macroreticular chelating resins containing mercapto groups.

## EXPERIMENTAL

### Preparation of Chelating Resins

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Macroreticular chelating resins containing mercapto groups (RSS, RGS-KSH, and RES) were prepared as shown in Scheme 1 (*1–3*).

***RSS.*** Commercial macroreticular styrene-divinylbenzene copolymer beads (20–60 mesh, Mitsubishi Kasei Kogyo Co. Ltd.) were used for the preparation of RSS. The copolymer beads (5 g) were chloromethylated with chloromethyl methyl ether (33 $cm^3$) at 0–5°C for 3 h in the presence of tetrachloroethane (5 $cm^3$) as swelling agent and of aluminum chloride (6.7 g) as catalyst. The chloromethylated copolymer beads (1 g) were treated with ethanolic potassium hydrogen sulfide solution (6 $cm^3$) at 50°C for 1 h.

***RGS-KSH.*** Macroreticular glycidyl methacrylate polymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane as diluent. The polymer beads (32–60 mesh) (1 g) were treated with a methanol solution of ammonium thiocyanate (35%) (6 $cm^3$) at room temperature for 48 h, and then the polymer beads (1 g) were treated with ethanolic potassium hydrogen sulfide solution (6 $cm^3$) at 50°C for 1 h.

***RES.*** 2,3-Epithiopropyl methacrylate (ETMA) monomer was prepared by the method reported previously (*2, 4*). Macroreticular ETMA-divinylbenzene copolymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane as diluent. The copolymer beads (32–60 mesh) (1 g) were treated with ethanolic potassium hydrogen sulfide solution (6 $cm^3$) at 50°C for 1 h.

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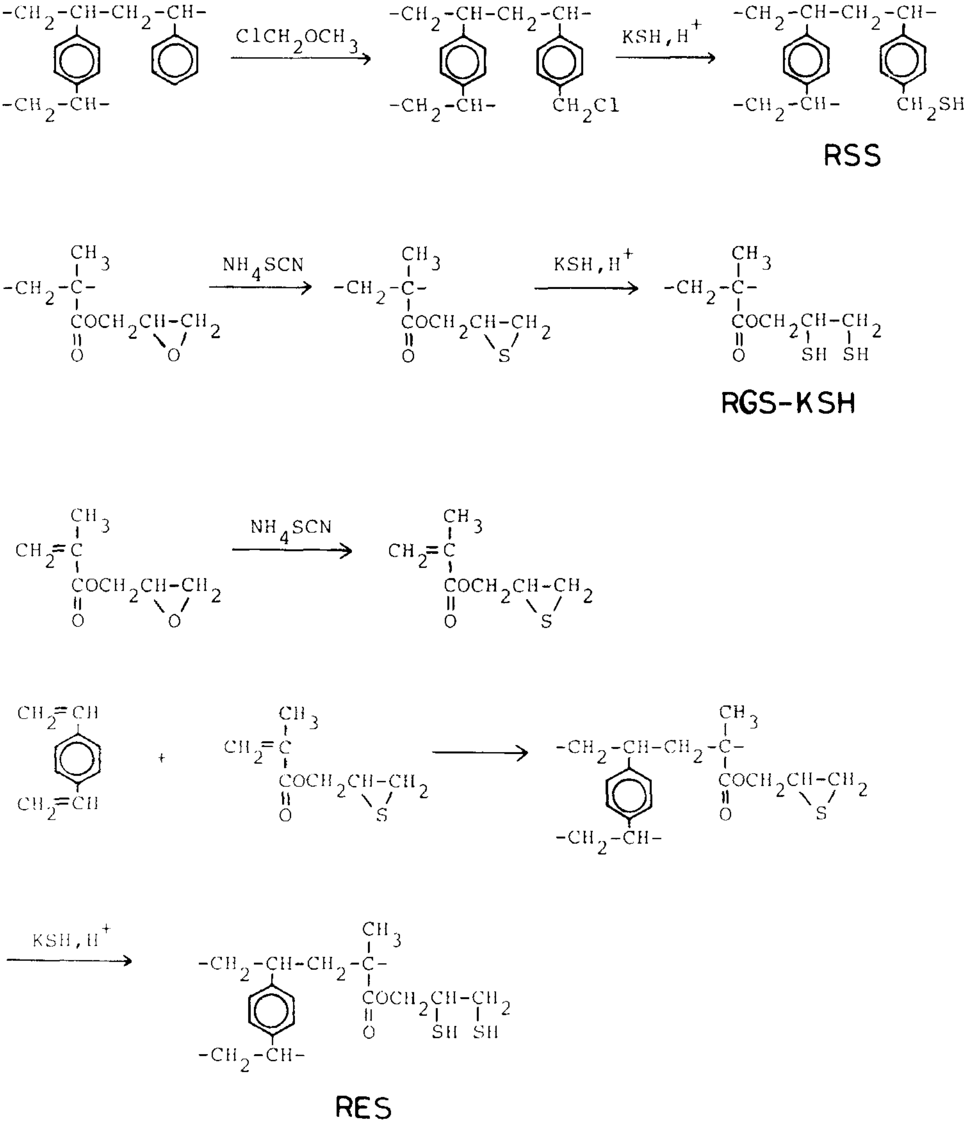

SCHEME 1. Preparation of chelating resins.

The three resulting resins (RSS, RGS-KSH, and RES) were washed with 1 mol/dm$^3$ of ammonia water and with deionized water until the wash water became neutral.

### Measurement of Adsorption Capacity for Mercury(II) Ion

In a glass-stoppered 100-cm$^3$ Erlenmeyer flask, 0.25 g of resin and 50 cm$^3$ of buffered mercury(II) ion solution (0.01 mol/dm$^3$, pH 2) were placed and then the mixture was allowed to stand at room temperature (about 25°C) for 48 h with occasional shaking. The amount of mercury(II) ion adsorbed on the resin was calculated by chelatometric determination of the mercury(II) ion concentration in the supernatant. Mercury(II) ion solution was prepared from reagent grade mercury(II) nitrate.

### *Measurement of Adsorption Ability for Arsenic(III) Ion*

***Batch Method.*** In a glass-stoppered 100-cm$^3$ Erlenmeyer flask, 0.125 g of the resin and 50 cm$^3$ of sodium arsenite solution (3 mg/dm$^3$ as As) were placed and then the mixture was shaken at 30°C for 24 h. The amount of arsenic(III) ion adsorbed was calculated from the result of quantifying arsenic(III) in the supernatant liquid by means of the spectrophotometric procedure based on silver diethyldithiocarbamate (5).

***Column Method.*** Two columns were prepared. One was packed with 2 cm$^3$ of RES (resin bed: 6 mm$\phi$ $\times$ 70 mm). The other was packed with 10 cm$^3$ of RES (resin bed: 10 mm$\phi$ $\times$ 128 mm). The solution containing arsenic ion was passed through the resin bed at a space velocity (SV) of 15–60 h$^{-1}$. Arsenic ion in the effluent was determined by means of spectrophotometry using silver diethyldithiocarbamate. Arsenic ion adsorbed on the column was eluted by passing 10 bed volumes of 2 mol/dm$^3$ sodium hydroxide solution containing 5% sodium hydrogen sulfide through the resin at a SV of 7.5 h$^{-1}$. Arsenic(III) ion solution was prepared from arsenic trioxide. A geothermal power waste solution which was sampled at the Ohtake Power Station in Kyushu, Japan, was also used for adsorption experiments of arsenic ion. The analytical data on the representative sample are listed in Table 1.

### Measurement of Adsorption Rate

One-half gram of the resin and 25 cm$^3$ of deionized water were placed in a 100-cm$^3$ three-neck flask. The resins in the flask were degassed under

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TABLE 1
Typical Compositions (mg/dm$^3$) and pH of Geothermal Water (*6*)

| | Ohtake Well No. | | | Ohtake Well No. | |
|---|---|---|---|---|---|
| Constituents | No. 9 | No. 10 | Constituents | No. 9 | No. 10 |
| As | 2.0 | 2.1 | F | 2.95 | 2.35 |
| Na | 1050 | 1030 | Cl | 1774 | 1738 |
| K | 132 | 124 | $HCO_3$ | 57 | 77 |
| Li | 4.79 | 4.73 | $SO_4$ | 145 | 193 |
| Ca | 28.4 | 29.7 | $HBO_2$ | 84 | 78 |
| Mg | 0.01 | 0.21 | $SiO_2$ | 531 | 433 |
| pH | 8.57 | 8.44 | | | |

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vacuum for 1 min. The mixture was allowed to stand overnight to permeate water into the resins. The flask was set in a fixed temperature bath. After 200 cm$^3$ of deionized water was poured into a flask, 25 cm$^3$ of sodium arsenite solution (3 mg/dm$^3$ as As) was added to the flask with vigorous agitation. In the case of the geothermal power waste solution, 225 cm$^3$ of the solution was added to the flask with vigorous agitation. After that, 2 cm$^3$ of the aqueous phase was collected with a volumetric pipet at fixed times and the concentration of arsenic ion in it was determined.

## RESULTS AND DISCUSSION

### Removal of Arsenic(III) Ion

The adsorption of arsenic(III) ion on the three chelating resins (RES, RGS-KSH, and RES) containing mercapto groups was examined under column operation which is a practical process for the removal and recovery of arsenic ion from geothermal power waste solution. The sodium arsenite solution (pH 6.2–6.5) containing 2.74–3.08 mg/dm$^3$ of arsenic(III) ion was passed through the resin columns at an SV of 15 h$^{-1}$. Table 2 shows the arsenic(III) leakage in the effluent. In the column method, RGS-KSH and RES exhibited satisfactory adsorption ability for arsenic(III) ion, indicating that the arsenic(III) ion concentration in the effluent was less than 0.01 mg/dm$^3$, whereas RSS showed poor affinity for arsenic(III) ion. This poor affinity of RSS for arsenic(III) ion is due to the low adsorption rate, as shown Fig. 1.

TABLE 2
Removal of As(III) in Aqueous Solution by the Use of the Chelating Resins[a]

| Effluent volume ($dm^3/dm^3$-resin) | As(III) leakage ($mg/dm^3$) | | |
|---|---|---|---|
| | RSS | RGS-KSH | RES |
| 10 | 0.73 | <0.01 | <0.01 |
| 20 | 0.64 | <0.01 | <0.01 |
| 40 | 0.73 | <0.01 | <0.01 |
| 60 | 0.98 | <0.01 | <0.01 |
| 80 | 0.99 | <0.01 | <0.01 |
| 100 | 1.15 | <0.01 | <0.01 |

[a] Resin bed: 20 $cm^3$ (10 mmϕ × 255 mm). Loading solution: As(III) 3 $mg/dm^3$, pH 6.2–6.6. Flow rate: SV 15 $h^{-1}$.

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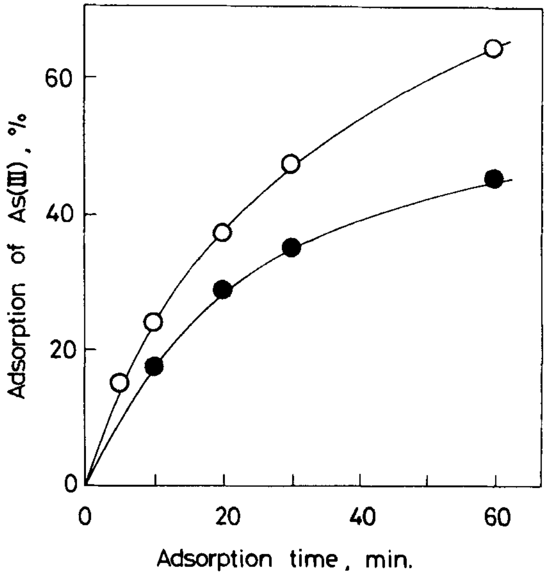

FIG. 1. Adsorption rate of As(III) on the chelating resins. (○) RES; (●) RSS; As(III) concentration, 3 $mg/dm^3$; 30°C.

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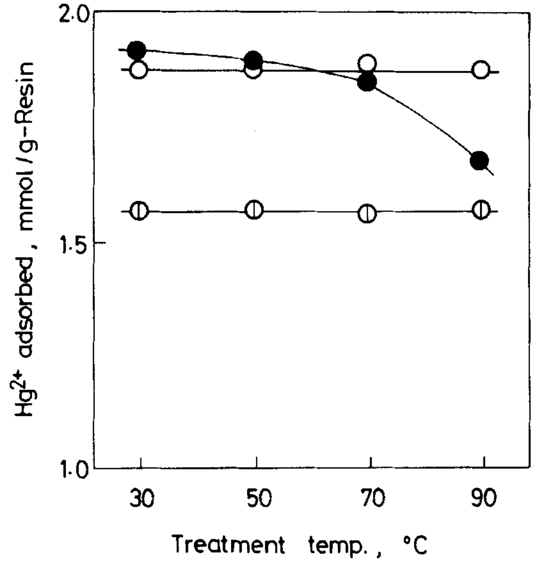

FIG. 2. Resistance of the resins against hot water. (⦶) RSS; (●) RGS-KSH; (○) RES; treatment time, 5 h.

## Resistance of the Resins Against Hot Water

A resin used for the removal of arsenic ion in hot geothermal solution must have resistance against hot water. Therefore, the $Hg^{2+}$ adsorption capacity of the three chealting resins which were treated with hot water was tested in order to evaluate their resistance against hot water. The results were shown in Fig. 2. It was found that RSS and RES had excellent resistance against hot water in comparison with RGS-KSH. RES also revealed a high affinity for arsenic(III) ion after it was treated with hot water (90°C) for a long time (48 h), as shown in Fig. 3.

From the results described above, it is concluded that RES is the most suitable resin for the removal of arsenic(III) ion in hot geothermal solution because of its high affinity for arsenic(III) ion and its high resistance against hot water in practical column operation.

## Effect of Coexistent Ion on the Adsorption of As(III)

Since the geothermal power waste solution contains large amounts of coexistent ions as shown in Table 1, the effect of coexistent ions on the

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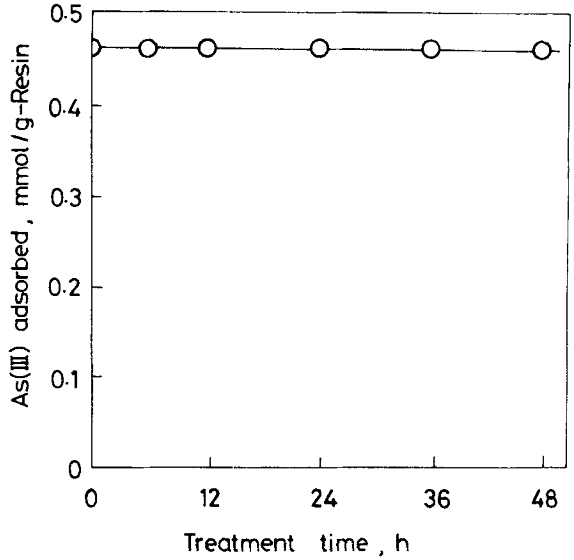

FIG. 3. Resistance of the RES against hot water. Treatment temperature: 90°C.

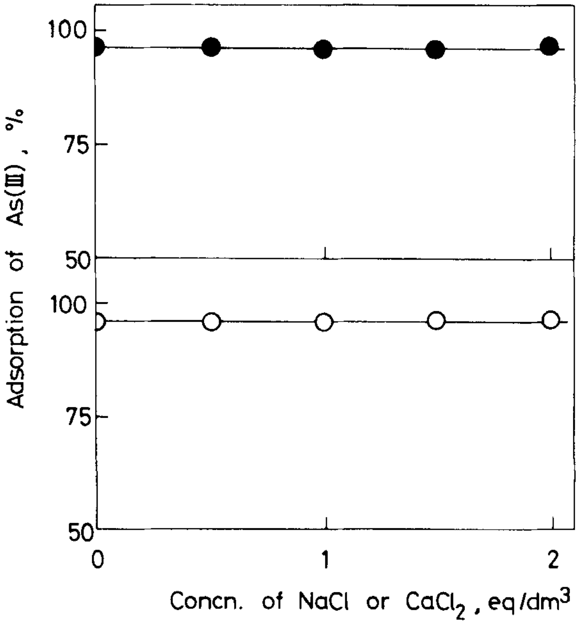

FIG. 4. Effect of coexistent ion on the adsorption of As(III). (○) NaCl; (●) $CaCl_2$; shaking time, 24 h; 30°C.

adsorption of arsenic(III) ion on RES was tested. Figure 4 shows the adsorption ability of arsenic(III) ion on RES in the presence of sodium chloride or calcium chloride. The adsorption of arsenic(III) ion on RES was not influenced by the presence of $Na^+$ or $Ca^{2+}$ in the concentration range of 0.5 to 2.0 equiv/$dm^3$. In the practical column method, the effect of coexistent ions on the adsorption of arsenic(III) ion on RES was also tested by passing 100 bed volumes of a sodium arsenite solution (As 3 mg/$dm^3$, pH 6.5) containing 10 g/$dm^3$ of sodium chloride through the column at an SV of 15 $h^{-1}$. The arsenic(III) ion concentration in the effluent was less than 0.01 mg/$dm^3$.

From these results it was found that the adsorption ability of RES for arsenic(III) ion is hardly affected by the presence of such coexistent ions as $Na^+$ and $Ca^{2+}$.

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## Recovery of Arsenic(III) Ion and Recycle

The recycle test of adsorption and elution of As(III) was examined under the column method by using 2 mol/$dm^3$ sodium hydroxide solution containing 5% sodium hydrogen sulfide as eluent. Figure 5

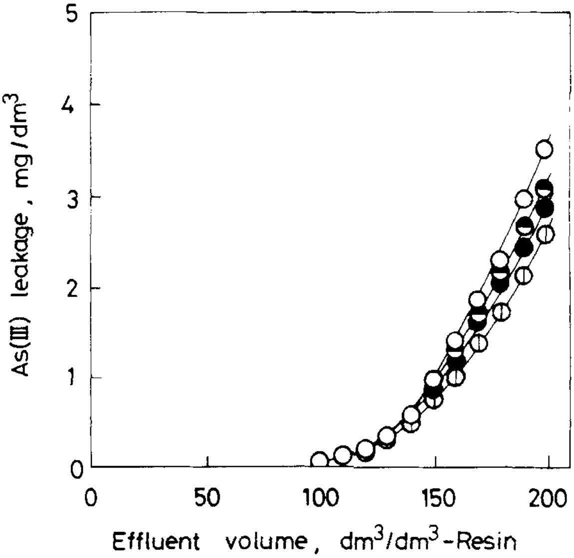

FIG. 5. Recycle test. Cycle number: (○) 1, (●) 3, (◓) 4, (⦶) 7. Resin bed: RES, 2 $cm^3$ (6 mmϕ × 70 mm). Loading solution: As(III), 20 mg/$dm^3$; pH 6.5–7.4. Flow rate: SVC 15 $h^{-1}$. Elution: 2 mol/$dm^3$ NaOH solution containing 5% NaSH, 10 $dm^3/dm^3$-resin, SV 7.5 $h^{-1}$.

shows the breakthrough curves of As(III) on repeated adsorption–elution procedure. A decrease of adsorption ability of RES for As(III) was not observed on repeated cycling.

From this result it was found that the recycle of adsorption and elution was satisfactory and that As(III) adsorbed on RES is effectively eluted by passing 10 bed volumes of 2 mol/dm$^3$ sodium hydroxide solution containing 5% of sodium hydrogen sulfide through the resin at an SV of 7.5 h$^{-1}$.

## Effect of Temperature on the Adsorption Rate of As

Figure 6 shows experimental results of the initial adsorption rate of arsenic ion on RES. The adsorption rate was measured by using a geothermal power waste solution (As 2.1 mg/dm$^3$, pH 6.8) at 30–90°C.

It was recognized that the adsorption of arsenic ion on RES is rapid at high temperature. This result suggests that, in order to remove arsenic ion from a geothermal waste solution by the column method, it is more effective to pass the hot geothermal waste solution directly through the resin bed.

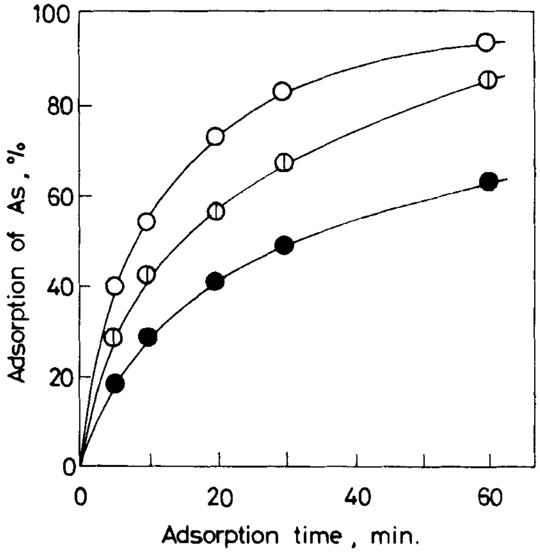

FIG. 6. Adsorption rate of As on the RES. (○) 90°C; (⦶) 60°C; (●) 30°C; Sample solution: geothermal water (As 1.9 mg/dm$^3$).

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TABLE 3
Removal of As from a Geothermal Power Waste Solution with RES[a]

| Effluent volume ($dm^3/dm^3$-resin) | As leakage ($mg/dm^3$) Column A | Column B | Column C |
|---|---|---|---|
| 20 | 0.05 | 0.03 | 0.04 |
| 40 | 0.02 | 0.04 | 0.06 |
| 60 | 0.04 | 0.05 | 0.06 |
| 80 | 0.03 | 0.03 | 0.05 |
| 100 | — | 0.02 | 0.05 |
| 120 | — | 0.06 | 0.05 |
| 140 | — | 0.05 | 0.04 |
| 160 | — | 0.04 | 0.04 |
| 180 | — | 0.05 | 0.06 |
| 200 | — | — | 0.04 |
| 220 | — | — | 0.06 |
| 240 | — | — | 0.05 |
| 260 | — | — | 0.06 |
| 280 | — | — | 0.05 |
| 300 | — | — | 0.04 |

[a] Flow rate: Column A, SV 15 $h^{-1}$; Column B, SV 30 $h^{-1}$; Column C, SV 60 $h^{-1}$. Resin bed: 10 $cm^3$ (10 mmϕ × 128 mm). Loading solution: Geothermal water (As 2.1 $mg/dm^3$, pH 8.6, 90°C).

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## Removal of Arsenic Ion from Geothermal Water

The removal of arsenic ion from a geothermal power waste solution was investigated under the column method. The geothermal waste solution was directly passed through three columns containing RES at space velocities of 15, 30, and 60 $h^{-1}$. Arsenic ion concentration, pH, and temperature of the waste solution were 2.10 $mg/dm^3$, 8.6, and 90°C, respectively. The results obtained at different flow rates are summarized in Table 3.

It was found that the removal of arsenic ion from the geothermal power waste solution was possible at a high flow rate which was favorable industrially, indicating that arsenic ion concentration in the effluent was less than 0.06 $mg/dm^3$ up to 300 bed volumes at an SV of 60 $h^{-1}$.

From the results mentioned above, it is proved that RES obtained by treating macroreticular ETMA-divinylbenzene copolymer beads with ethanolic potassium hydrogen sulfide solution are of practical use for the removal and recovery of arsenic ion from geothermal power waste solution.

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