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Sulfide Removal by Strong Basic Anion Exchanger

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As the raw water containing sulfide ion such as S^{2-} or HS^- causes various troubles to be used for chemical factories, we studied the possibility of these ion removal by strong basic anion exchanger. We examined this problem using several anion exchangers, but they have no great difference in their capacities and then we studied the conditions of the bed, of the operation and of the regeneration of resins using mainly Duolite A-40.

The capacity of OH form was found to be greater than Cl form, and the pH of sample solution in either case of S^{2-} or HS^- was favorable at acid side. The concentration of S^{2-} had no great effect on the resin capacity between 0.067–0.013%. The fatigue of Duolite A-40 was smaller than that of Duolite A-41. When we regenerate the resin to Cl form, we found that the solution containing NaCl and small quantity of alkali (pH≒11) was effective.

When the volume of resin in a tube was increased by increasing the bed height, the breakthrough curves were not parallel to that of little resin volume, that is to say the width of exchange zone enlarged. This phenomenon means that the equilibrium value in solution is considerably large.

1. Introduction

If the raw water or waste water of chemical factories contains sulfide ion, there happens some troubles such as the corrosion of apparatus, bad smelling and etc.

Treaties of air passing is usually used to remove sulfide ion but we can remove only to the degree of about 5 ppm of the ion by this method. For the purpose of attaining more effectiveness, we must adopt the air passing lime methode[1] or chlorine treating or precipitating method with iron salt.

Strong basic anion exchanger whose active radical is consisted of quaternary ammonium base (≡NX) can absorb weak mineral acid such as H_2S, and Kunin[2] reported that some Amberlite resin—strong basic anion exchanger—can be used to this purpose.

We attempted to establish a industrial method of removing of sulfide ion from the waste solution of a factory using anion exchange resin. Firstly we tested fundamentally the removal of sulfide ion from the solution containing Na_2S or H_2S. And the kinds of resin, form of resin, particle size, height of resin bed, number of usage, solution velocity, ion concentrations of sample solutions, kinds of solutions and the conditions of regeneration were tested. We found that this resin—quaternary ammonium basic resin, Duolite A-40—is satisfactorily used to remove sulfide ion from solution and regenerate the resin.

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Fig. 1 Photographs of resin

Photo (1) Duolite A—40, 16～32mesh (991～495μ) (observed value from photograph, 1200～520μ)
×50 by reflected ray

Photo (2) Duolite A—41, 16～32 mesh
×20 by passed ray

Photo (3) Dowex-2, 16～32 mesh
(observed value from photograph, 1100～400μ)
×20 by reflected ray

Photo (4) Amberlite IRA—400, 16～32 mesh
(observed value from photograph, 700～300μ)
×50 by reflected ray

Photo (5) Amberlite IRA—401, 16～32 mesh
(observed value from photograph, 1170～500μ)
×20 by reflected ray

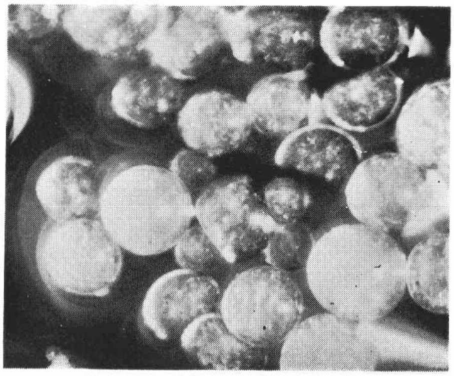

Photo (3)

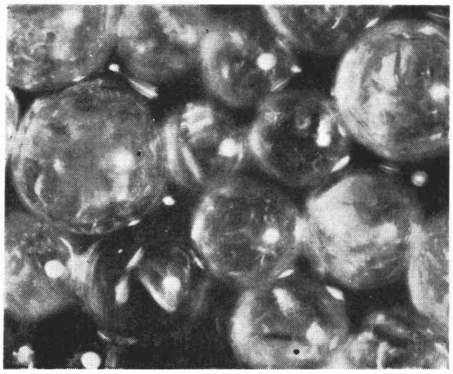

Photo (1)

Photo (4)

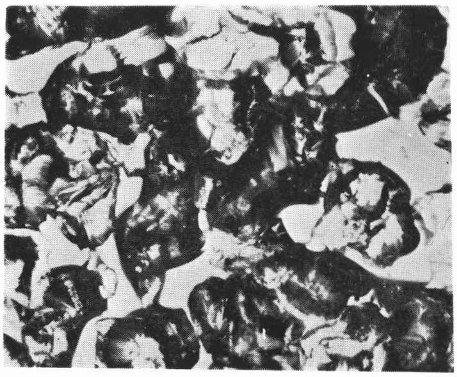

Photo (2)

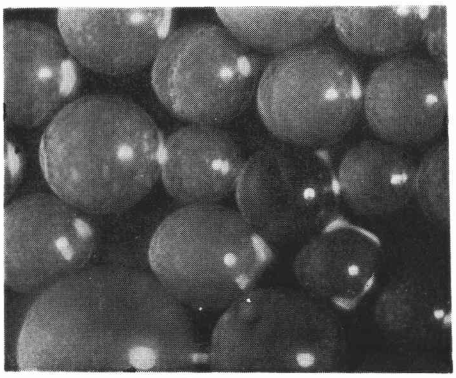

Photo (5)

2. Samples of Resin and Experimental Methods

2-1. Samples of resin and their characters

Samples of resin which we used were tabulated in Table 1 with their characters. The total capacities of resins in this table are given by references. The porosities were observed by us, and that of Duolite A-41(granular) was largest, and the others indicated about same values.

Table 1. Resins used

	Shape of resin	Color	Total capacity, (meq/ml) (OH-resin)	Porosity, (%) (16~32 mesh)
Duolite A-40	spherical	yellow-white	1.2	32
Duolite A-41	granular	reddish-brown	0.8 (quaternary) 1.4 (tertiary)	40
Dowex-2	spherical	yellow-white	1.1	29
Amberlite IRA-400	spherical	pale yellow	1.0	28
Amberlite IRA-401	spherical	yellow	0.8	32

The photographs of these resins are shown in Fig. 1.

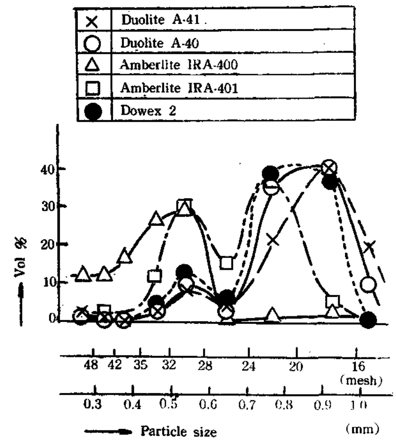

Fig. 2. Particle size distribution.

The results of observations of particle size distribution of the resins are plotted in Fig. 2. As shown in graph, Amberlite IRA-400 indicates some different distribution from others, namely it has more proportion of small particle (under 28 mesh), and other four resins are mixed with 16~24 mesh and 28~35 mesh resins.

2-2. Experimental methods

The glass tube whose inside diameter is 9.7, 18, 20 or 25 mm was used in these experiments, and the Na_2S solution or H_2S solution was charged on the top of these glass tube. Breakthrough curves were obtained by measuring the pH values of the effluents using glass electrode pH meter. The breakthrough point of sulfide ion was determined by the change of pH value and also by calorimetric method using dimethyl-paraphenylen-diamine[3] or nitro-plussid natrium as indicator. The former indicator can detect S^{2-} 0.0000005 g per 1 cc, and the latter can detect S^{2-} 0.000002 g per 1 cc. (The latter indicator was used only in Fig. 7 experiment.)

3. The Results of Experiment

(A. Conditions of bed)

3-1. Breakthrough curves of various resins.

In the glass tube of i.d. 9.7 mm, resin (16~32 mesh) was packed to the height of

21 cm (packed volume of resin was 15 cc). To this column $Na_2S \cdot 9H_2O$—0.5% solution (S^{2-} 0.067%) was charged at the velocity of 3 cc/min (0.064 cc/cm²/min). These results are indicated in Fig. 3.*)

As shown in the figure, the inclinations of curves of Duolite resins are less sharp than Amberlite resins. And the brerkthrough capacities of S^{2-} of these resins are calculated as 0.14~0.28 meq/cc resin.**)

3-2. Effect of resin form (Cl form or OH from)

(The following experiments were done by using Duolite A-40.)

OH form and Cl form of the resin (each 16~32 mesh) were studied with the solution of S^{2-} 0.067 and 0.027%. Fig. 4 indicates these results. The throughput capaci-

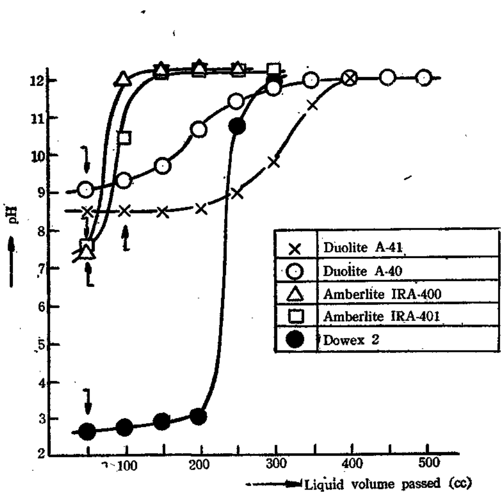

Fig. 3. Breakthrough curves of various resins tube dia. 9.7 mm, resin volume 15 cc, particle size 16~32 mesh, temp. 15°C S^{2-} concentration 0.067 %, 3 cc/min. ↱S^2 breakthrough point by D.P.P.

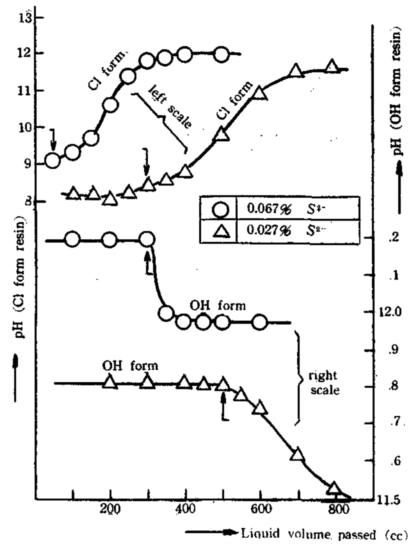

Fig. 4. Effect of resin form Duloit A-40, 16~32 mesh, tube dia. 9.7 mm, resin vol. 15 cc, temp. 15°C, 3 cc/min.

ty of OH form resin is 0.8 meq/cc resin, 0.14 by Cl form resin (S^{2-} 0.067%), and 0.56 meq/cc resin by OH form and 0.36 by Cl form (S^{2-} 0.027%).

3-3. Effect of particle size.

These results are indicated in Fig. 5. The smaller particle size is, the larger throughput capacity was obtained.

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*) The initial pH value of Dowex-2 is low because it was regenerated by HCl, while the others were regenerated by NaCl.

**) These values are smaller than those of Table 1, because these resins are Cl form and liquid velocity is somewhat fast.

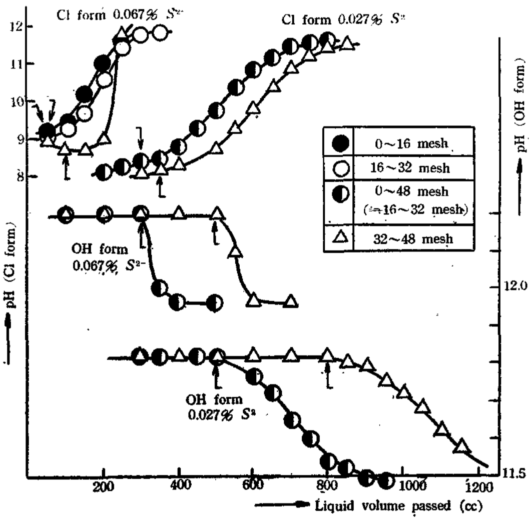

Fig. 5. Effect of particle size
Duolite A-40, tube dia. 9.7 mm, resin vol. 15 cc, 3 cc/min, 15°C

3-4-1. Bed height and tube diameter (variation of resin volume).

In Table 2, the results are indicated when bed height is changed at constant diameter and liquid velocity. In Table 3, the results are indicated when tube diameter is changed at constant bed height and liquid velocity.

Table 2. Effect of bed height, Duolite A-40, 16~32 mesh (Cl form) diameter 9.7 mm, S^{2-} 0.065% 26°C, 3 cc/min

Bed height (cm)	Resin volume, V (cc)	Throughput volume Q (cc)
20.8	15	50
33.7	24.9	90
60.0	44.5	170
83.5	63	250
100.0	75	300

$$Q=2.5\,V^{1.12} \qquad \text{(1)}$$

Table 3. Effect of tube diameter, Duolite A-40, 16~32 mesh (Cl form) bed height 21 cm, S^{2-} 0.065% 26°C, 3 cc/min

Glass tube diameter (mm)	Resin volume, V′ (cc)	Throughput volume, Q′ (cc)
9.7	15	50
18	50	150
20	65	200
25	100	300

$$Q'=4.0\,V'^{0.96} \qquad \text{(2)}$$

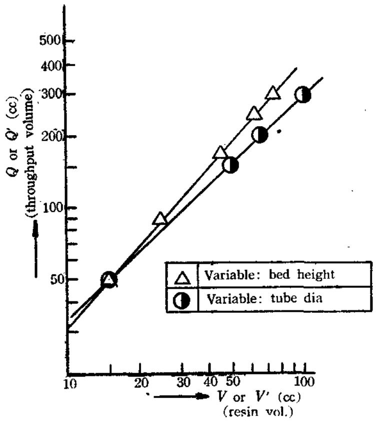

Fig. 6 Resin volume vs. throughput volume Duolite A-40, 16~32 mesh tube dia. 9.7 mm, 26°C S^{2-} 0.065%, 3 cc/min

As shown in Fig. 6, if we plott resin volume V and V′ in abscissa and throughput volume Q and Q′ in ordinate from Table 2 and 3, we get two straight lines, and we get formulas (1) and (2) correspond to these lines respectively. The small difference between inclinations of two lines would be perhaps due to their wall effects.

3-4-2 Shape of throughput curve at varions resin volume.

In Table 2 the results are shown when we used i.d. 9.7 mm glass tube and the bed height was changed. Farthermore we used i.d. 22 mm tube and the throughput curves were observed at various bed height. These results are shown in Fig. 7.

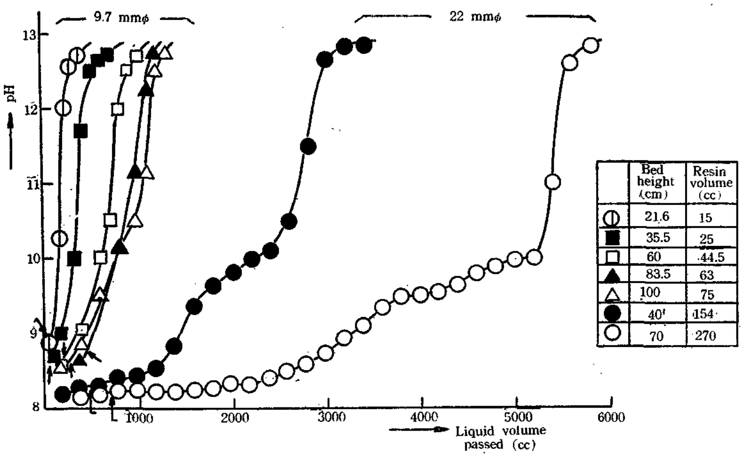

Fig. 7 Ehape of throughput curve at various resin volume [↑—>detection point by nitro] {Duolite A-40, 16~32 mesh, S^{2-} 0.067%, 3 cc/min, 26°C

When the bed height is increased (namely resin volume is increased), its throughput curve is not same as that of low bed height. The width of exchange zone becomes enlarged. This would be due to the fact that equilibrium concentration of S^{2-} in the solution could not be lowered at such a liquid velocity.

The relation between pH value of effluent and S^{2-} concentration (ppm) is shown in Fig. 8.

3-5 Effect of repeated exhaustion and regeneration.

15 cc of wet Doulite A-40(Cl) resin was exhausted with $Na_2S \cdot 9H_2O$—0.2% solution (S^{2-} 0.027%) at the liquid velocity 3 cc/min, and regenerated by the most suitable

method after described (1N NaCl + alkali). The first capacity was 0.34 meq/cc-resin, and after 8 cycles it was 0.32 and its value was continuously about constant to 11th cycle. The decreasing velocity is so slow that it can be used repeatedly.

Doulite A-41 resin was also tested by the same method above. At the beginning of test this resin showed same capacity as A-40, but its capacity decreased about 5% in 3rd run and the test was continued to 5th run with same capacity.

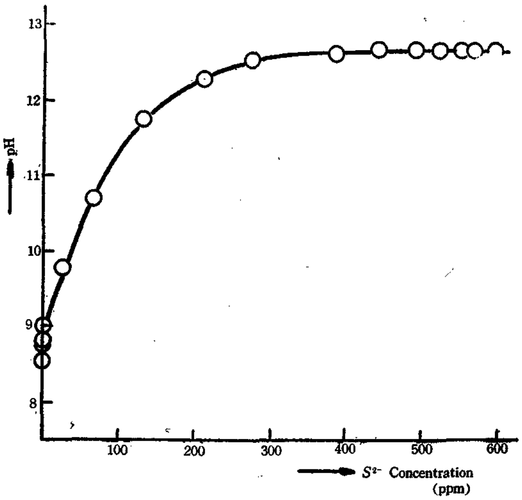

Fig. 8 Relation between pH value and S^{2-} concentration (ppm)

The yellow-white Duolite A-40 was colored pale brown at 11th run, but this pale brown returned its original color by standing of about 10 days in water after regeneration. But Duolite A-41 was colored black at 1st run, and it did not return its original color after regeneration.

(B. Conditions of run)

3-6 Effect of liquid velocity.

Doulite A-40 (Cl) (16~32 mesh) (regenerated with HCl) was exhausted with the solution containing S^{2-} 0.067% at the liquid velocity of 0.5, 1.0, 3.0 cc/min (0.01, 0.02, 0.06 cc/cm²/min). These results were shown in Fig. 9. These throughput volume were 200, 150, 50 cc respectively and calculated capacities are 0.56, 0.42, 0.14 meq/cc-resin. They decreased in inverse proportion with their space velocity (S.V.) 2, 4, and 12. (Fig. 10.)

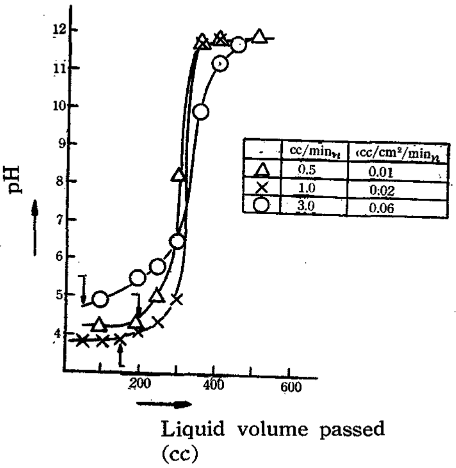

Fig. 9 Eflect of liquid velocity
Duolite A-40, 16~32 mesh,
tube dia. 9.7 mm,
resin volume 15 cc, 15°C
S^{2-} 0.067%

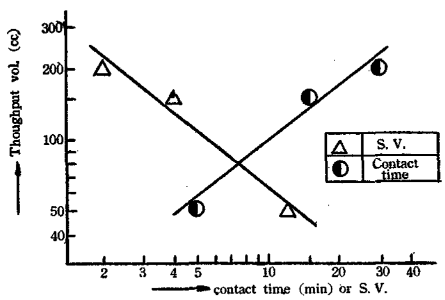

Fig. 10 Through put volume vs. contact time or space velocity

3·7 Effect of S^{2-} concentration.

The tested varieties of S^{2-} concentrations in the sample solution were 0.067, 0.027 and 0.013% using $Na_2S \cdot 9H_2O$. The resin used was 15 cc of wet Duolite A-40 (OH) (the particle sizes were almost 16~32 mesh and oversize of 16 and (−32 +48) mesh are small quantity). These breakthrough volumes were 300, 500, 1200 cc, and the capacities were 0.81, 0.56, 0.65 meq/cc-resin, mean capacity 0.67 meq/cc-resin.

3·8 Comparison of Na_2S and H_2S solution.

15 cc of wet Duolite A-40 (OH) (16—32 mesh) was exhausted with $Na_2S \cdot 9H_2O$—0.2% solution or H_2S solution of nearly equal S^{2-} concentration. The results are given in Table 4.

Table 4 Results of Na_2S and H_2S
solu. temp. 29°C liq. velocity 0.06 cc/cm²/min

sample solu.	S^{2-} content (%) obs.	pH	S^{2-} break-through pt. (cc)	absorbed S^{2-} from throughput vol. obs.		desorbed S^{2-} from 1N NaOH regenerant, obs.	
				(mg)	(meq/cc resin)	(mg)	(meq/cc resin)
Na_2S	0.0283	12.2	465	131.6	0.55	130.2	0.54
H_2S	0.0208	4.8	1270	264.6	1.10	269.8	1.12

Breakthrough point of Table 4 or Table 5 was obtained by detection with nitro-plussid Na.

Next, Na_2S sol. and H_2S sol. were prepared in same pH, and the results obtained are given in Table 5.

Table 5 Results of Na_2S and H_2S in same pH
{solu. temp. 29°C
{liq. velocity 0.06 cc/cm²/min

resin form	sample solu.	pH	S^{2-} content (%)	S^{2-} breakthrough point (cc)
Cl	Na_2S	13.2	same as Table 4	200
	H_2S			150
	Na_2S	8.9		400
	H_2S			550

It is known that the effect of pH of sample solution is important. Large capacity of H_2S shown in Table 4 is perhaps due to overwhelming large amount of HS^- compared to S^{2-},[4] also as shown in Table 5 HS^- of both solutions become rich approaching to acid side and then the exchanged amount increase.

3·9 Conditions of regeneration.

The resin which absorbed S^{2-} or HS^- from Na_2S or H_2S was regenerated with the solution of 1N NaCl, 1N NaOH or 1N NaCl+NaOH (pH value about 11). The results are given in Table 6.

Table 6. Conditions of regeneration
Duolite A-40, 15cc, 16-32 mesh

absorbed solu.	regenerant solution	required regenerant solution, (cc) [by nitroplussid Na]	temp. of regenerant solution (°C)	liq. velocity (cc/cm²/min)
Na_2S	1N NaCl	100	25	0.06
	1N NaOH	100		
	1N NaCl (pH=11.4)	100		
Na_2S	1N NaCl	200	10	0.06
	1N NaOH	350		
	1N NaCl (pH=10.8)	150		
H_2S	1N NaCl	150	28	0.06

When the temp. is 25°C three regenerants have same ability to regenerate the resin, but at 10°C, 1N NaCl+NaOH (pH≒11) showed most strong ability.

The velocity with which S^{2-} is desorbed by 1N NaOH is great at the beginning of desorption—namely 92% of absorbed S^{2-} was desorbed at 1st 50 cc of tot. 400 cc regenerant (Na_2S absorbed resin), and 94.7% was desorbed at 1st 50 cc of tot. 300 cc regenerant (H_2S absorbed resin).

4. Conclusion

According to the above results we recognize that Duolite A-40 resin can be used to catch S^{2-} satisfactorily from a little amount of Na_2S or H_2S dissolved in water and also be regenerated to repeat the run and so that this process can be used for industrial purpose.

Acknowledgements

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