CONTRIBUTIONS TO THE ION EXCHANGE TREATMENT OF WASTE WATERS CONTAINING CYANIDE

THE BINDING OF METAL COMPLEX CYANIDES ON STRONG BASIC ANION EXCHANGE COLUMN FROM NEUTRAL AND SLIGHTLY ALCALINE SOLUTIONS

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Considering the steadily increasing exhaustion of natural water supplies, the requirements i.e. the official prescriptions against the waste liquor treatments are becoming more and more rigorous in industrialized countries all over the world in the last decades.

In the galvanic industry, where cyanide baths after galvanizing of the metal substances washing water of high volumes are to be used, the treatment of the waste liquors containing cyanide ions are very important. The elimination of the poisonous cyanide ions is, in general, carried out by an oxidative process using chlorine as oxidant in a slightly alkaline medium [1]. Sometimes the precipitation method using iron(II)sulphate is also used. For the elimination of the metal impurities precipitation (which can be carried out at the same time with chlorination) and settling of the precipitate are usual. Considering the low concentration of the impurities and the small rate of settling, large volume tubes are necessary.

First used in fifty years was also the ion exchange technique for the purification of cyanide containing waters, in Germany [2]. The ion exchange method has the advantages, that it does not need large space, it can be used continuously, the obtained regenerate liquid contains the impurities approximately at the same level and at a much higher concentration than the original, hence the treatment can be carried out much easier. The main advantage of the ion exchange technique was that the purified water of significant amount could again be used in a factory.

For investigation of the binding properties of cyanide and metal complex cyanide ions on strong basic anion exchange column of different forms, experiments were carried out using sodium cyanide and zinc-, copper- and cadmium cyano complex containing stock solutions. In the experiments the effluent portions obtained after the resin columns were analysed and the break through curves were constructed.

Experimental

Stock solutions

Sodium cyanide solution 178 mg/l (3.63 mval/l)

Copper(I)cyano complex containing solution. 4.82 g of sodium cyanide and 1.869 g of copper(I)cyanide were dissolved in water and the obtained clear solution diluted to 25 l. By analysing the last solution there was found 70 mg/l (1.43 mval/l) free sodium cyanide and 53 mg/l copper bound in cyano complex of composition $Na_3[Cu(CN)_4]$.

Zinc(II)cyano complex containing solution. 5.13 g of sodium cyanide and 1.486 g of zinc oxide were dissolved in the presence of each other in water and the solution was diluted to 25 l. According to the analysis of the obtained solution there was found 205 mg/l (4.19 mval/l) sodium cyanide (free and complexed together) and 47.7 mg/l zinc all being in the form of $Na_2[Zn(CN)_4]$. According to calculation the alkaline solution also contained 1.47 mval/l sodium hydroxide.

Cadmium(II)cyano complex containing solution. 5.002 g of sodium cyanide and 1.449 g of cadmium oxide were dissolved in water and the solution was diluted to 25 l. By analysis of the obtained solution 200 mg/l (4.08 mval/l) sodium cyanide (free and complexed together) and 45 mg/l of cadmium were found. According to calculation the total amount of the cadmium was complexed in the form of $Na_2[Cd(CN)_4]$ and also 0.806 mval/l sodium hydroxide was present in the solution.

Analytical procedures

For the determination of the cyanide ion argentometric titration was used. The determination of copper content was carried out by the chelatometric method using 0.01 M sodium ethylenediamine tetraacetate as titrant and 1-(2-pyridylazo)-2-naphtol as indicator. The determination was carried out after oxidative decomposition of the cyano complex with sulphuric acid and ammonium peroxy disulphate. The determination of the zinc ion was carried out directly in the cyanide containing solutions chelatometrically using the above indicator. For determination of cadmium also direct chelatometric titration in the presence of xylenol orange indicator was used.

Ion exchange columns. In all experiments the same type columns of 6 mm inner diameter were used. The height of the resin bed was 10 cm. The used, strongly basic resin, was Varion AD (Nitrokémia, Hungary) of polystyrene-divinylbenzene type of grain size 20—50 mesh. The capacity of the columns were determined by the usual method and were found to be 3.4 mval. To bring the columns in the required form of OH, Cl, SO_4 or CO_3, 1 N sodium

hydroxide, 2 N sodium chloride, sulphate and carbonate solutions were used, respectively. Finally the columns were washed with distilled water.

Saturation experiments. They were carried out by using the stock solutions. The flow rate was always controlled and kept at about 3 cm/Min. The effluent was collected in 10 ml fractions, which were analysed. On the basis of the obtained data the break through curves were constructed. The concentrations found by analysis in the fractions were plotted against the volume of the effluent.

Regeneration experiments. Were carried out after the saturation experiments using the corresponding 1 N alkali or 2 N salt solutions. The effluent portions were analysed as above.

Results and discussion

On the basis of the preliminary experiments it was found that a considerable absorption of the cyanide and also of metal complex cyanide ions took place on the OH- and Cl-form resin beds only. The break through curves obtained by the saturation experiments on OH and Cl-form resin columns can be seen in figures 1—4.

The simple cyanide ions break through the columns quickly without any significant absorption (Fig. 1). The cyanide ion appeared in the effluent at 326 and 218 ml, respectively, to the OH-form and Cl-form columns. Considering the concentration of the influent solution one could calculate that at the break through points the capacity of the columns was utilized only in 34.7 and 23.2 per cent, respectively. At the end of the saturation process the utilizations were found to be 88.2 and 96.0 per cent.

The regeneration of the columns using 1 N sodium hydroxide and 2 N sodium chloride solutions were found to be complete in both cases at 200 ml of the regenerants.

If the copper(I)cyano complex containing solution was poured on the OH-form and Cl-form resin columns the break through points of the free cyanide ions appeared at 610 and 220 ml, however, those of copper at 1600 and 1550 ml, respectively. Using the diagram of the break through curves (Fig. 2) by graphical integration the ion uptake of the total saturated columns were calculated. It was found that about 3.4 mval cyanide ion and 1.65 mval of copper(I) cyanide were absorbed on both columns. Considering the total capacity of the resin columns (3.4 mval) and the absorbed quantities of the two species, one must assume that by decomposition of the three valent complex, anion being in the influent solution, the absorption of a divalent complex of composition

$$[Cu(CN)_3]^{2-}$$

took place. The stronger absorbable divalent complex ions displaced nearly quantitatively the less absorbable simple cyanide ions.

The utilizations of the OH- and Cl-form resin columns for the divalent complex ions were at the break through points of the copper 79 and 76.5 per cent, respectively.
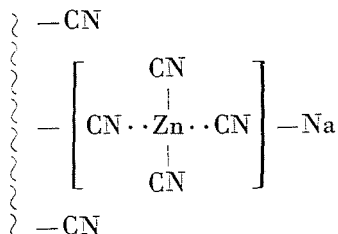
The regeneration of the columns were found to be complete by using 280 ml of 1 N sodium hydroxide and 300 ml of sodium chloride.

The break through curves of the zinc cyano complex containing solution can be seen in Fig. 3. The slopes of the curves were greater if OH-form resin column instead of Cl-form column was used. On the basis of the data of the diagram the total ion uptake by the resin column was also calculated. It was found that on the OH-form column (and very similarly on the Cl-form column)

9.6 mval CN^- ion (free and complexed together)

2.04 mmol zinc ion

were bound. Considering the total capacity of the column (3.4 mval) it must be assumed that 1.4 mval of the resin capacity was occupied by cyanide ions and the remainder 2 mval by the ca. 2 mmol tetracyano zinc(II) complex ions. Hence the latter were bound only with their one valence in the following form:

$$
\begin{array}{l}
\} -CN \\
\} \\
\} \quad \left[\begin{array}{c} CN \\ | \\ CN \cdot \cdot Zn \cdot \cdot CN \\ | \\ CN \end{array} \right] -Na \\
\} \\
\} -CN
\end{array}
$$

Thus, the $Na_2[Zn(CN)_4]$ complexes which are in the solution absorbed on the resin as monovalent ions and they share the sites of the resin with the simple cyanide ions.

Presuming zinc complexes are monovalent, the utilization of the OH- and Cl-form resin columns were at the break through points of the zinc: 48.3 and 38.6 per cent, respectively.

For the complete regeneration of the columns 400 ml of 1 N sodium hydroxide and 300 ml of 2 N sodium chloride were necessary.

The absorption behaviour of the cadmium complex was found to be similar to that of zinc. By a similar calculation using the data of the Fig. 4 it was found that at total saturation

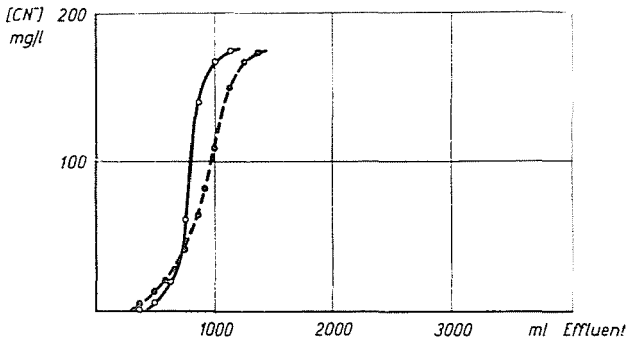6.12 mval CN^- ion and

0.94 mmol Cd

Fig. 1. Break through curves of the cyanide ion
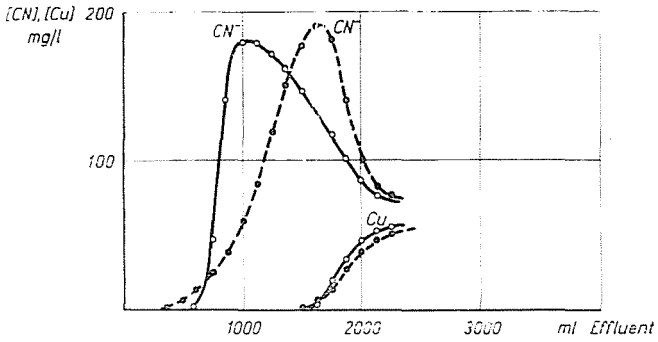———— OH-Form, - - - - Cl-form anion exchange column

Fig. 2. Break through curves of the cyanide and copper
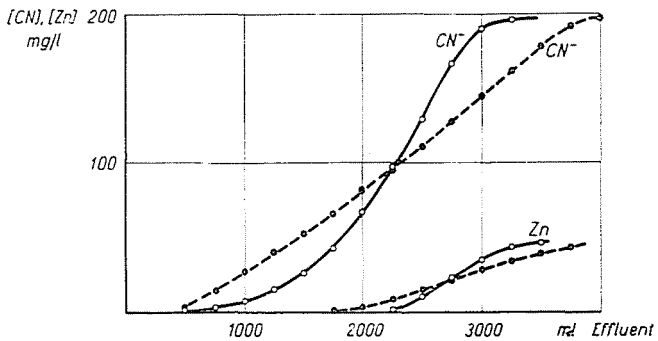———— OH-Form, - - - - Cl-form anion exchange column

Fig. 3. Break through curves of the cyanide and zinc
———— OH-form, - - - - Cl-form anion exchange column

were absorbed on the columns. Presuming that tetracyano cadmium complexes were present in the solution, one might suggest that 0.94 mmol of $Na_2[Cd(CN)_4]$ complex was absorbed on the resin as monovalent ion and beside that ca. 2.46 mval of simple cyanide ion.
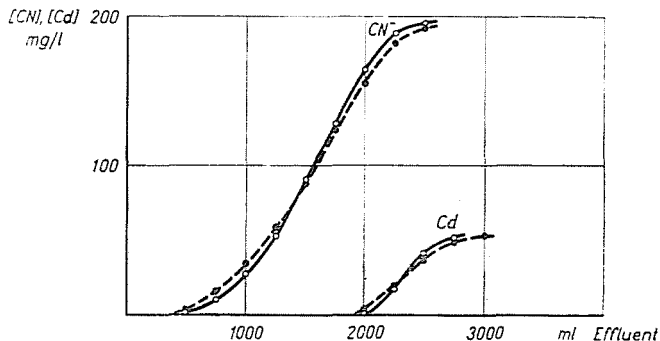

Fig. 4. Break through curves of the cyanide and cadmium
———— OH-form, - - - - Cl-form anion exchange column

The found phenomena (i.e. the absorption of the tetracyano complexes by one valence) are surprising because the hexacyanoferrate(III) and hexacyanoferrate(II) ions absorb on anion exchange resin without decomposition by three and four valences, respectively.

Presuming cadmium complexes are bound by one valence, the utilization of the OH- and Cl-form resin columns are at the break through points of the cadmium: 22.9 and 23.5 per cent, respectively.

On the basis of the experiments it can also be established that the order of the absorbability of the metal complexes is the following one:

$$Cu > Zn > Cd$$

From neutral or slightly alkaline dilute solutions the simple cyanide ions can be absorbed only with a very low efficiency. Among the complex bound metals, copper can be absorbed most successfully. The absorbabilities of zinc and cadmium complexes are lower.

Summary

The absorption of the cyanide and the copper(I)-, zinc(II)- and cadmium(II)cyano complexes from dilute solutions on strong basic anion exchange columns was investigated. It was found that the absorption of the copper(I)cyano complex took place in the form of $[Cu(CN)_3]^{2-}$ ions, while in the absorption of the zinc and cadmium complexes the monovalent binding of the tetracyano complex compounds was suggested.

Literature

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2. KRUG, J.: Galv. Techn. **55**, 32 (1964).

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