Solvent Extraction of Nickel-Cobalt Chloride Mixtures with Furfural

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THE UTILITY of furfural as an extraction solvent for the separation of the more common metals was investigated. Furfural has previously been shown to be effective in the separation of heavy metal chelates (*1*, *2*). The present work demonstrates the applicability of furfural to the selective separation of cobalt ions from nickel ions using calcium chloride as a complexing agent.

Other extractive processes have been investigated (*3*–*8*) but furfural may prove advantageous because of its relative stability, demonstrated selectivity, and low cost. The complexing agent required is inexpensive.

Nickel and cobalt were chosen for study because of the separation problem existing in the processing of lateritic ores (*5*). In these ores, cobalt and nickel are found in the approximate ratio of 1 part of cobalt to 10 parts of nickel. The metal chlorides are easily prepared form these ores.

EXPERIMENTAL

All extractions were single stage, using equal volumes of freshly distilled furfural and aqueous metal chloride solution. Prior to extraction, 30 grams of anhydrous calcium chloride was added to each 50 ml. of aqueous metal salt solution.

Cobalt(II) chloride and nickel(II) chloride solutions were prepared and analyzed by standard wet methods.

Solutions were analyzed after extraction by determination of the count rate using $Ni^{63}Cl_2$ and $Co^{60}Cl_2$ tracers and a conventional scaling counter. An aluminum β-ray shield was used for discrimination between beta and gamma radiation in the case of the mixed chlorides.

The nickel content of the furfural phase was so low in all cases as to be almost undetectable by counting techniques, hence the distribution coefficient for $0.5M$ nickel(II) chloride was determined by the dimethylglyoxime method, eliminating the statistical error inherent in radiochemical analysis at these extremely low levels.

DISCUSSION

While nickel and cobalt chlorides alone give poor separation on furfural extraction, cobalt(II) chloride and hydrochloric acid form a complex which is extractable with furfural, *n*-butyl tetrahydrofurfuryl ether, and methyl tetrahydrofuran. Unfortunately, all of these solvents are rather soluble in the aqueous phase; also, high concentrations of hydrochloric acid destroy furfural rapidly. Calcium chloride, magnesium chloride, and ammonium chloride accomplished the same results without solvent destruction. For economic reasons, furfural and calcium chloride are the materials of choice. Also, furfural has low solubility in a concentrated calcium chloride solution.

Preliminary studies indicated that a 24 to 44% solution of calcium chloride is required to complex the cobalt chloride adequately. Nickel(II) chloride apparently does not complex to any appreciable extent.

Table I gives the results for extraction of cobalt(II) chloride with furfural. The aqueous feed contained 30 grams of calcium chloride per 60 ml. of stock solution.

The results of Table I show that the distribution coefficient of cobalt(II) chloride is constant over a considerable concentration range. It is reasonable to assume that this trend holds for somewhat lower concentrations than those measured.

No similar table is presented for nickel because the radiation level of the furfural layer was essentially that of the background, indicating that distribution did not occur. This was true over the entire range of concentrations, which was the same as that for cobalt in Table I. Because of this, a conventional dimethylglyoxime analysis was run on $0.5M$ nickel(II) chloride after extraction. The distribution coefficient was found to be 0.003. The nickel found in the furfural may be due to entrainment, rather than to solubility.

These results indicate that the extraction should effectively remove cobalt from nickel. To determine whether the presence of nickel affected the distribution coefficient of cobalt, mixed solutions were extracted with the results shown in Table II.

Because of the statistical error in the count rates at the low radiation levels employed, the distribution coefficient is presumed to be a constant.

Based on a distribution coefficient of 0.003 for nickel and 1.0 for cobalt, a separation factor of the order of 3×10^2 is calculated. On this basis, it is calculated that a four-stage extraction of a 10 to 1 nickel-cobalt mixture would give nickel concentrates containing less than 10 parts of cobalt to 1000 parts of nickel. A similar three-stage extraction of the cobalt pregnant extract would afford cobalt of 99+ % purity.

Nickel and cobalt are immediately and completely removed from the metal-bearing furfural layer by extraction with water. While some furfural will dissolve in the water extract, it is easily recovered by steam stripping. Cobalt and nickel may then be recovered from the appropriate

Table I. Furfural Extracts Cobalt Chloride from Aqueous Solutions

Cobalt, Grams per Liter			
	After extraction		
Original soln.	Aqueous	Organic	Distribution Coeff.
60.472	30.236	30.236	1.00
30.236	15.280	14.956	0.98
6.071	3.035	3.035	1.00
3.006	1.550	1.456	0.94
1.474	0.737	0.737	1.00

Table II. Cobalt Extraction Is Unchanged in Presence of Nickel

Metal in Feed, G./L.		Wt. Ratio,	Co after Extraction, G./L.		Co Distribution	Probable Error,
Ni	Co	Co to Ni	Raffinate	Extract	Coeff.	%
30.871	3.024	0.0979	1.514	1.509	1.0	3.2
30.871	1.515	0.0490	0.756	0.756	1.0	5.3
30.871	0.760	0.0246	0.384	0.376	1.0	10.1
30.871	0.377	0.0122	0.177	0.200	1.1	8.6

aqueous extracts or raffinates by precipitation as sulfides. Another approach to metal recovery is electrodeposition.

The calcium chloride solution remaining after deposition of nickel from aqueous raffinates could be recycled to effect necessary process economy.

CONCLUSIONS

Furfural is an effective selective solvent for the separation of cobalt from nickel when present as chlorides in aqueous solutions.

Calcium chloride is an excellent complexing additive. High purity nickel and cobalt may be obtained via a process based on this extraction system.

The general utility of furfural as an extraction solvent for metal separations has been further substantiated.

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RECEIVED for review September 19, 1960. Accepted December 30, 1960.

Tables of Ozone Properties

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OZONE is a highly active, allotropic form of oxygen. It has been known since 1785, the year in which van Marum observed the formation of this gas in an electric spark discharge in oxygen. Schoenbein recognized ozone in 1840 as a new substance. Soret showed in 1866 that the chemical composition of ozone is that of triatomic oxygen.

At ordinary temperatures, ozone is a gas, is light blue in color, and has a characteristic pungent odor from which its name was derived from the Greek word ozein, to smell. The odor permits recognition of ozone in concentrations down to about 0.1 p.p.m. Gaseous ozone is a highly active, irritating, oxidizing substance. It is characterized by its strong oxidizing power and by the tendency to revert to molecular oxygen according to the reaction

$$O_3 \rightarrow 3/2\ O_2$$

The rate of reaction depends upon the temperature, pressure, and concentration of the ozone. The reaction proceeds slowly at ordinary temperatures, but fairly quickly, even to the velocity of thermal explosion, at elevated temperatures. In addition, the reaction is catalyzed by many sensitizers. Low temperatures contribute to the conservation of ozone.

In the liquid phase, ozone has an indigo-blue color. At temperatures around 90° K. (−183° C.), liquid ozone may be kept without noticeable decomposition for long periods. Fast warming to the boiling point or rapid cooling causes explosions. The liquid ozone must be evaporated or frozen, therefore, very slowly with appropriate precautions. Liquid ozone can be supercooled readily.

Solid ozone has a deep blue-violet color. A layer 0.2 to 0.5 mm. is transparent, but solid ozone in a layer 1 mm. thick is almost opaque. Solid ozone (at 77.35° K.) was compressed to 22.5 atm. without any difficulty. Slight impact and slight friction at that temperature did not cause an explosion.

Gaseous, liquid, or solid ozone explodes easily if exposed to heat, spark, flame, or shock. When working with highly concentrated ozone, improper handling may cause a violent explosion. A knowledge of the properties and safety pre-