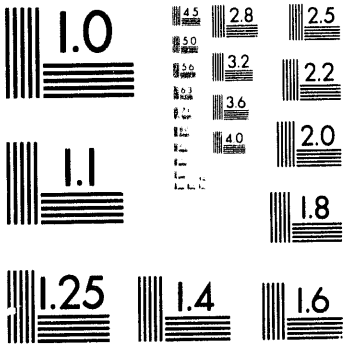
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WSRC-RP-93-1325

CARBOLLIDE SOLUBILITY AND CHEMICAL COMPATIBILITY SUMMARY (U)

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DOE Contract No. DE-AC09-89SR18035

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Savannah River Technology Center

WSRC-RP-93-1325

Keywords: Carbollide,
In-Tank Precipitation

Retention: Lifetime

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Carbollide Solubility and Chemical Compatibility Summary (U)

SUMMARY

The cobalt dicarbollide anion (CDC) has been investigated for the possible replacement of tetraphenyl borate anion (TPB) for precipitation of cesium in SRS High Level Waste (HLW). The solubility of the cesium CDC in 5 M salt solutions and the reactivity with caustic have been studied extensively. The solubility of CsCDC in a mixture of 4 M sodium nitrate and 1 M sodium hydroxide is ~2 x 10^{-3} M at 40 °C. Furthermore, the CDC decomposes in 1 M sodium hydroxide solution with apparent first order kinetics with a half-life of 7.3 days at 60 °C and 94 days at 40 °C. Tank temperatures are currently estimated to approach 60 °C during the ITP filtration cycle.[1] This solubility and rapid decomposition of the CDC under highly alkaline conditions and high temperature would require increasing the quantity of CDC and non-radioactive cesium which must be added, increasing the cost of production. Increasing the quantity of CDC would necessitate recovery of the material, probably using a solvent extraction system. Due to the large amount of nonradioactive cesium which must be added, the total amount of precipitate formed exceeds that for TPB precipitation. Also, formation of sodium and/or potassium precipitates compete with cesium salt precipitation in 5 M salt solutions at lower temperature (<30 °C). Decomposition generates hydrogen, which may lead to process complications.

INTRODUCTION

The In-Tank Precipitation (ITP) process decontaminates radioactive waste in Tank 48 by precipitating radioactive cesium with TPB, $(C_6H_5)_4B^-$, and adsorbing radioactive strontium on sodium titanate

(ST). The solids are separated from the salt solution by crossflow filtration. Alternate chemicals for precipitation of cesium are being examined. One of these chemicals is the cobalt dicarbollide anion (CDC), $Co(C_2B_9H_{11})_2^-$. Use of this compound would prevent generation of benzene and it is postulated that the precipitate may be directly compatible with borosilicate glass.

Prior to proposing use of this compound as a replacement for TPB, the compatibility and effectiveness of CDC must be examined. The waste solutions typically contain large amounts of sodium nitrate and sodium hydroxide, and smaller amounts of many compounds. Compatibility with these compounds is necessary to evaluate the technical viability of CDC in ITP. Solubility of CsCDC and the potassium and sodium salts are critical to the potential use of CDC as a precipitating reagent in SRS HLW. Higher solubility of CsCDC would require excess CDC to force the cesium out of solution. Addition of a large excess of CDC could be complicated by precipitation of the sodium and potassium salt and competing with cesium precipitation.

A SCUREF contract was placed with Clemson University (CU) for this work. The compatibility was examined by researchers in SRTC, CU, and Indiana University (IU). Solubility was examined by SRTC and CU. This work was funded by the Department of Energy Office of Technology Development (Technical Task Plan SR-1320-07).

The Clemson work was conducted by examining disappearance of the UV/Vis absorption band characteristic of CDC. The IU work consisted of observing the B-11 NMR (Nuclear Magnetic Resonance) peaks for CDC and boric acid. The SRTC work corroborated the observations of the CU and IU studies. This was done by adding cesium CDC in excess of its solubility at 25 °C to sodium hydroxide solutions. The solutions were then maintained at elevated temperature (60 °C). Control solutions were maintained at room temperature. At periodic intervals, the solutions were cooled, filtered, and analyzed. Cesium and boron solubility was observed to increase with decomposition as expected, and yielded rates quite similar to those reported by CU.

EXPERIMENTAL

Samples of cesium cobalt dicarbollide were synthesized according to literature references. Three replicate samples of the recrystallized solid were submitted for analysis (Table 1).

Table 1
Average Composition of CsCDC

Component	Observed wt%	Theoretical wt%
Cs	26.8 (±20%)	29.1
Co	12.9	12.9
B	46.0	42.6

A 2.66 mM sample of the CsCDC (0.0182 g) was added to a 1.0 M sodium hydroxide solution (15 mL) prepared by addition of 0.5818 g sodium hydroxide in deionized water (15 mL). The solution was placed in a Teflon™ bottle and submerged in a constant temperature water bath at 60 ± 1 °C. The temperature was recorded with a calibrated thermometer twice per day. Samples were withdrawn at various intervals (47, 72, 96, 163, and 261 hours). The samples were cooled to room temperature and stirred for 48 hours prior to filtering. Filtration was accomplished with 0.2 micron Gelman PTFE disposable filter discs at 24 ± 1 °C.

Samples were prepared with 2.0 and 3.0 mM CsCDC in 1.0 M sodium hydroxide in Teflon™ bottles. These were placed in the same water bath and aliquots withdrawn after decomposition was nearly complete. The aliquots were stirred at room temperature for at least 48 hours prior to filtering. Filtration was accomplished with 0.2 micron Gelman PTFE disposable filter discs at 24 ± 1 °C. Analytical results reported in Tables 1 and 2 were obtained using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) with an error of ±20%. Analytical results reported in Figure 1 was obtained by Atomic Absorption (AA), those reported in Figures 2 and 3 were obtained by ICP-Emission Spectroscopy and are all ±10%.

RESULTS

The samples were withdrawn from the 2.66 mM CsCDC/1.0 M NaOH solution at intervals which allow observation of the decomposition. The solubility of CsCDC in 1.0 M NaOH was determined to be 1.14 ±0.16 mM at 25 °C. In determining the decomposition rate, the soluble portion of the material was assumed to remain constant (i.e. 1.14 mM) because there was excess solid CsCDC. As the soluble CsCDC decomposes, more CsCDC dissolves to compensate and the cesium concentration of the soluble fraction increases (Figure 1). The boron and cobalt concentrations should also increase. The boron solubility was observed to increase (Figure 2), but the cobalt was inconsistent (Figure 3). This is attributed to the appearance of a black/brown solid which adheres to the bottle, which has been identified as CoO(OH).

Similar results were observed for the 2.0 and 3.0 mM CsCDC in 1.0 M NaOH solutions. The solubility of cesium was seen to increase after decomposition (Table 2). Samples from the solution which contained a total of 2.0 mM CsCDC were collected after decomposition was nearly complete, allowing all of the cesium to become soluble. Samples from the 3.0 mM CsCDC solution were only partially decomposed after 169 hours and yielded a calculated cesium solubility of 2.59 mM. The calculated value is based on the solubility plus the quantity predicted to decompose according to the Arrhenius equation. After 360 hours, essentially all of the CsCDC was decomposed and the cesium became completely soluble.

Table 2
Composition of CsCDC/NaOH Solutions at 60 °C

Hours	2.0 mM Observed [Cs] (mM)	2.0 mM Theoretical [Cs] (mM)	3.0 mM Observed [Cs] (mM)	3.0 mM Theoretical [Cs] (mM)
0	1.12 (±20%)	1.14	1.13 (±20%)	1.14
169	2.13	2.0	2.65	2.59
360	1.88	2.0	2.84	3.0
550	2.12	2.0	2.91	3.0

DISCUSSION

The CU researchers had determined the rate equations for the decomposition of CDC using UV/Vis spectrometry.[2] It was not known whether a new species which was capable of precipitating cesium was formed, or if the material completely decomposed. Studies using B-11 NMR at IU suggested that the boron cage completely disintegrates and forms the hydroxide ion of boric acid, $B(OH)_4^-$. Rate constants from NMR data are not highly accurate, but suggested a similar rate to that observed by UV/Vis. It was necessary to conduct experiments using elemental analysis techniques to confirm the observations of both studies.

The rate expression reported[2] for the decomposition of CDC is

$$\text{Rate} = k[CDC][OH]^{1.25} = k_o[CDC]$$

and Arrehnius expression

$$\ln(k_o) = 34.4 - 1.33 \times 10^4 \ (1/T)$$

where T is in °K. The observed apparent first order kinetics with CDC concentration allows calculation of the half-life of the material in solution. In 1.0 M sodium hydroxide the half life is:

7.3 days @ 60 °C

94 days @ 40 °C

As predicted by these equations, the solubility of cesium increases during the decomposition (Figure 1). The equations were used to calculate a theoretical cesium solubility. The cesium is soluble above the solubility limit (1.14 mM) after 49 hours, and continues to increase to near the maxiumum amount possible after 250 hours. Analytical techniques for small amounts of cesium in 1.0 M sodium by Atomic Absorption spectroscopy can exhibit errors due to matrix effects; however, analysis of the boron in solution yields an excellent correlation with the value predicted from the

equations (Figure 2). It can be concluded that the equations are valid, based on these analyses.

Results from the boron analyses suggest that all of the boron decomposes to a soluble form during the decomposition. This result, coupled with the observation of boric acid as the only soluble boron-containing species in the NMR data, suggests that the rate-limiting step in the reaction is extraction of the first boron. The remainder of the boron/carbon cage quickly disintegrates thereafter.

The results of the cobalt analysis are not consistent with formation of a soluble cobalt species during decomposition. This is consistent with the observation of a brown/black insoluble material which adhered to the interior of the Teflon™ bottles. A similar solid was observed in previous studies and has been identified as containing CoO(OH) by X-ray diffraction.[2] Since this material would be expected to be removed by filtration of the samples, the results are consistent with formation of CoO(OH) precipitate.

The solubility of CsCDC in 1.0 M NaOH solution was determined by preparation of several samples containing various amounts of excess insoluble CsCDC and maintaining them at room temperature. The average solubility at 24 ± 1 °C is 1.14 ± 0.16 mM, based on B, Cs, and Co concentrations, where the error is the standard deviation. Solubility did not measurably change on any of the samples when maintained at room temperature for up to 23 days, consistent with the calculated rate constants at 25 °C from the Arrehnius equation.

The solubility of CsCDC in "5 M salt" solution was studied by CU[2] and SRTC[3] researchers. The CU simulant contained sodium hydroxide (1.0 M) and sodium nitrate (4.0 M). The SRTC simulant used to corroborate the data was a salt solution simulant which contains predominantly 1.4 M NaOH, 2.4 M $NaNO_3$, 0.9 M $NaNO_2$, and 0.5 M $NaAlO_2$ and nonradioactive and radioactive cesium. Dilution of this mixture with water was necessary to prevent competitive precipitation of NaCDC. The CU simulant was analyzed using UV/Vis spectrophotometry. The Ksp reported for CsCDC in this media was 5 x 10^{-6} M^2 at 40 °C. This is consistent with the value obtained by SRTC on simulated salt solution using radioactive Cs tracer studies; Ksp = 3.8 x 10^{-6} M^2 at 25 °C.[3] At 25 °C and high sodium concentration (~5 M) sodium (or potassium) cobalt dicarbollide also precipitated, yielding poor DF values for cesium. The sodium salt did not precipitate in a 3.9 M sodium solution (total hydroxide and nitrate) at 25 °C, and the solubility product was estimated to be Ksp(NaCDC) = 1.3 x 10^{-2} M^2.

The impact of the high solubility on processing SRS HLW would be that very large amounts of CDC^- would be needed to achieve the required Decontamination Factor (DF), and precipitation of NaCDC

would compete with cesium precipitation. To obtain a DF of 40,000 a staged precipitation, addition of non-radioactive cesium and temperature control would be required (Table 3).

Table 3
Theoretical Two-stage CDC Decontamination Factor

	Stage 1	Stage 2
Initial [Cs] (non-rad + rad)	0.15 mM	0.089 mM
Initial [CDC]	0.0	56 mM
Added [Cs]	10 mM	35 mM
Added [CDC]	66 mM	30 mM
% Cs precipitated	99.1	99.7
Stage DF	113	357
Cumulative DF	113	40600

In this example, the effect of sodium precipitation has not been addressed. At high CDC concentration NaCDC precipitation would be in competition with cesium precipitation, particularly at room temperature, to yield lower decontaminations. Also, the addition of a total of 96 mM CDC (33 g) of NaCDC per liter of salt solution adds significantly to the cost to process the waste. Based on the catalog price of CDC starting material (o-carborane) the cost would be ~$30/g for CDC, which would be ~$1000 per liter of salt solution. Nearly half of the CDC could be recovered, presumably in a solvent recovery system, although this has not been developed. The amount of nonradioactive cesium which must be added is 300 times higher than the initial amount of cesium present, generating a large amount of waste to be treated. This amount of precipitated material would exceed that currently projected for TPB precipitation of cesium and potassium.

With the large concentrations of CDC needed to facilitate cesium precipitation, a significant amount would be lost to decomposition during processing. The current estimates for Tank 48 indicate that the TPB slurry may exceed 60 °C during filtration.[1] In 1.0 M NaOH at 60°C, the half-life is calculated to be 7.3 days. The current projection for ITP operation indicates that the TPB precipitate could remain in the tank for 100 days prior to washing,[4] although it is not at 60 °C during the entire period.[1] It could be assumed that little decomposition would take place during washing due to lowering hydroxide concentrations. Use of CDC would require shorter processing times and addition of excess CDC to compensate for the decomposition and still maintain a high DF.

Reducing the tank temperature to 40 °C would increase the half-life to 94 days, but this would require the installation of a heat exchanger and chiller. At 40 °C a significant amount of CDC would decompose with the current tank configuration due to the long

cycle time (>100 days). Washing the precipitate after each filtration batch would reduce decomposition, but would decrease the overall plant capacity. Inadvertent cooling of the solution to less than 30 °C would increase precipitation of NaCDC, reducing the DF. A third tank would also be required, as the filtrate requires a second chemical addition and filtration before it is fully decontaminated. Both filtration steps may be accomplished with a reconfigured ITP facility or the Late Wash facility, depending on filtration rates. The current shielding requirements on ITP filtrate would need to be evaluated to ensure that the filtrate from the first precipitation is adequately shielded.

Byproducts generated during the CDC decomposition have been examined. Species identified by CU but not quantified include boric acid, cobalt hydroxide oxide, and hydrogen. The impact of these species on the process has not been fully examined. The boric acid is expected to remain soluble and would be in the decontaminated salt solution. The cobalt hydroxide oxide is insoluble and is expected to remain with the filtered precipitate. The hydrogen gas is expected to cause flammability problems in tanks. (For example: if the hydrogen rate were 0.5 mole per mole of CDC decomposed, a half-full vessel at 60 °C would reach the Lower Flammability Limit in 29 hours) It is also likely that residual CDC removal from decontaminated salt solution would be required to prevent hydrogen flammability problems in saltstone. The high caustic content (>1 M NaOH) and high temperature (~60 °C) of the waste during saltstone processing and current lack of flammability controls would necessitate removal.

CONCLUSIONS

Use of the cobalt dicarbollide anion to precipitate radioactive cesium in SRS HLW is impractical. To achieve a DF comparable to that from TPB a large amount of CDC must be added to the waste, due to the high solubility of CsCDC. The cost of the CDC would be prohibitively high. The amount of precipitated waste generated would increase due to the addition of a large amount of nonradioactive cesium. Competitive precipitation from sodium at ambient temperatures and high CDC concentrations would become problematic. Decomposition of CDC would require equipment modifications to lower processing temperatures and shorten processing times. A third tank would be needed to carry out a second precipitation step. A method and process would need to be developed to remove CDC from decontaminated salt solution. Generation of decomposition byproducts such as hydrogen and cobalt hydroxide oxide could be problematic.

QUALITY ASSURANCE

SRTC research on this project was addressed in a Task QA Plan (WSRC-RP-93-1091) and Technical Task Plan (WSRC-RP-93-1012). Research conducted by SCUREF-subcontracted institutions was governed by the SCUREF QA program. The SRTC research corroborated

the SCUREF-subcontracted institutions' research, verifying the decomposition rates and solubilities.

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3. "Experimental Studies with Cobalt Dicarbollide Anion: Progress Report", Karraker, D.G., WSRC-RP-93-1263, August 16, 1993.

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Figure 1. Observed vs. Theoretical Cs Concentrations

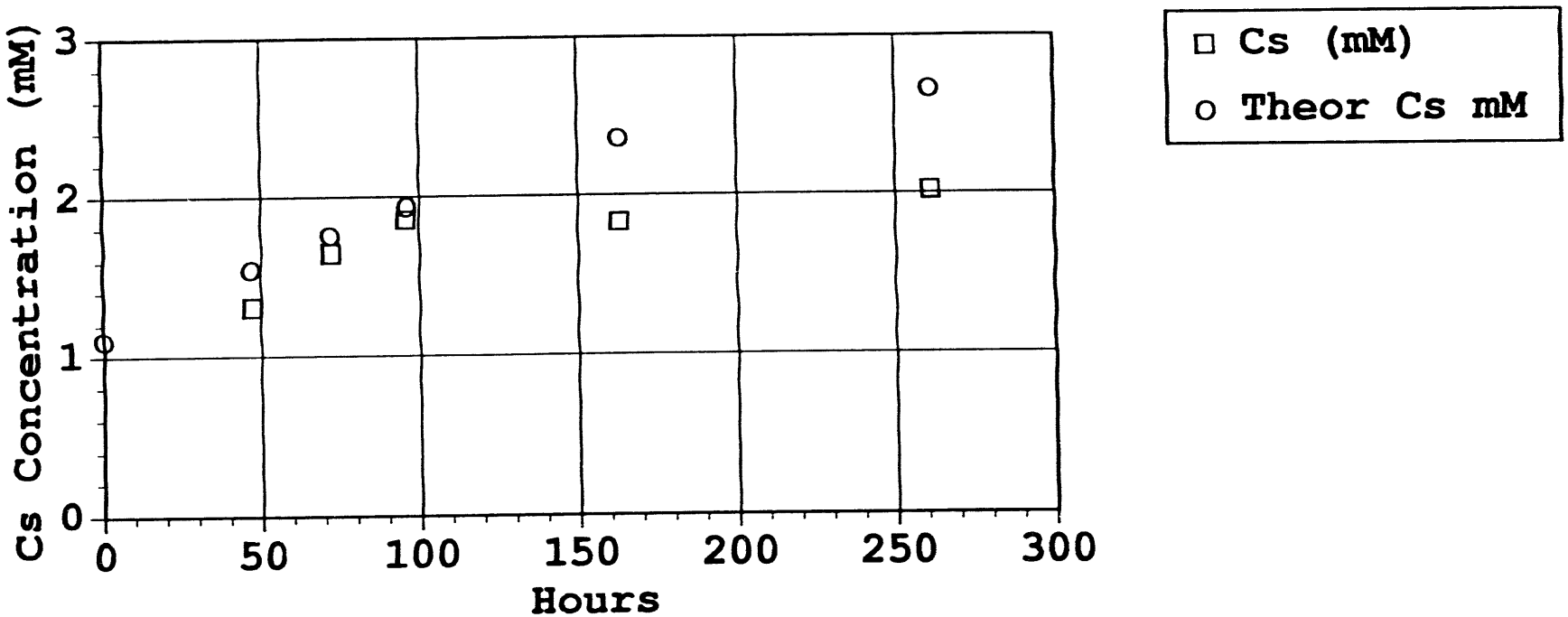


Figure 2. Observed vs. Theoretical B Concentrations

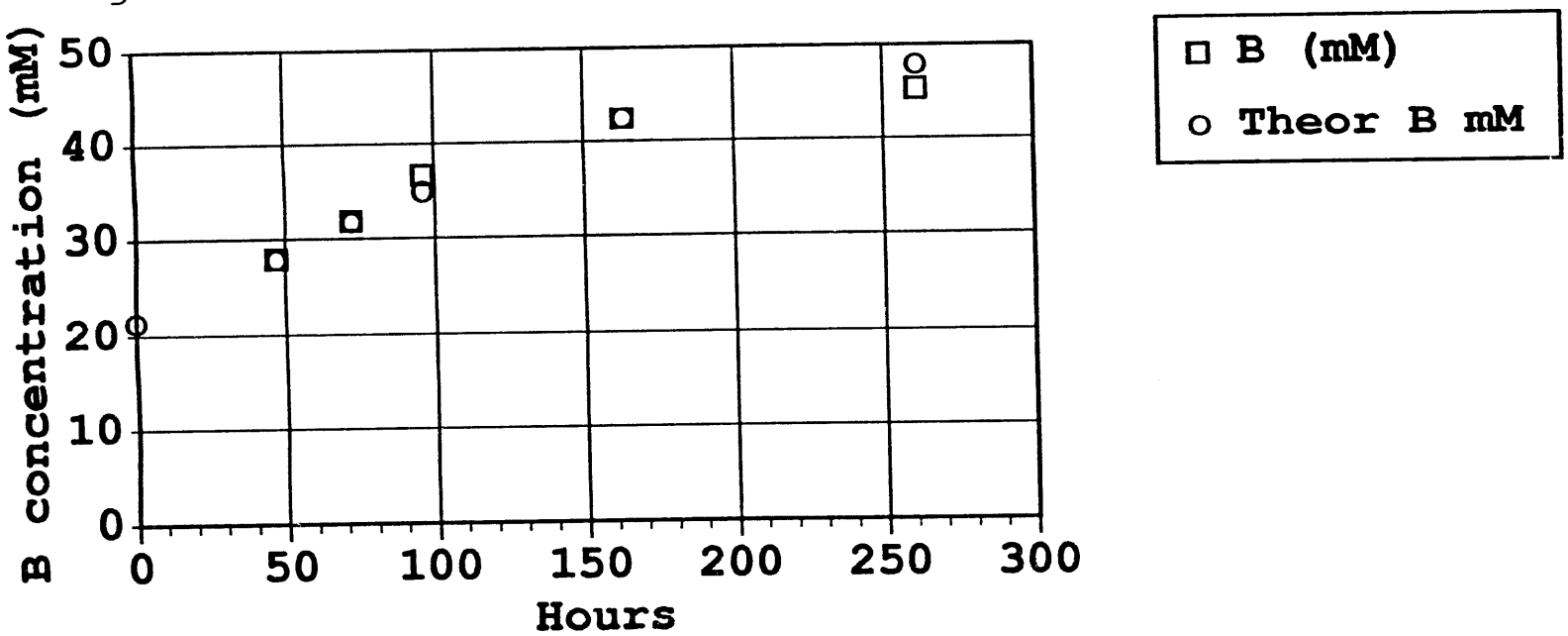
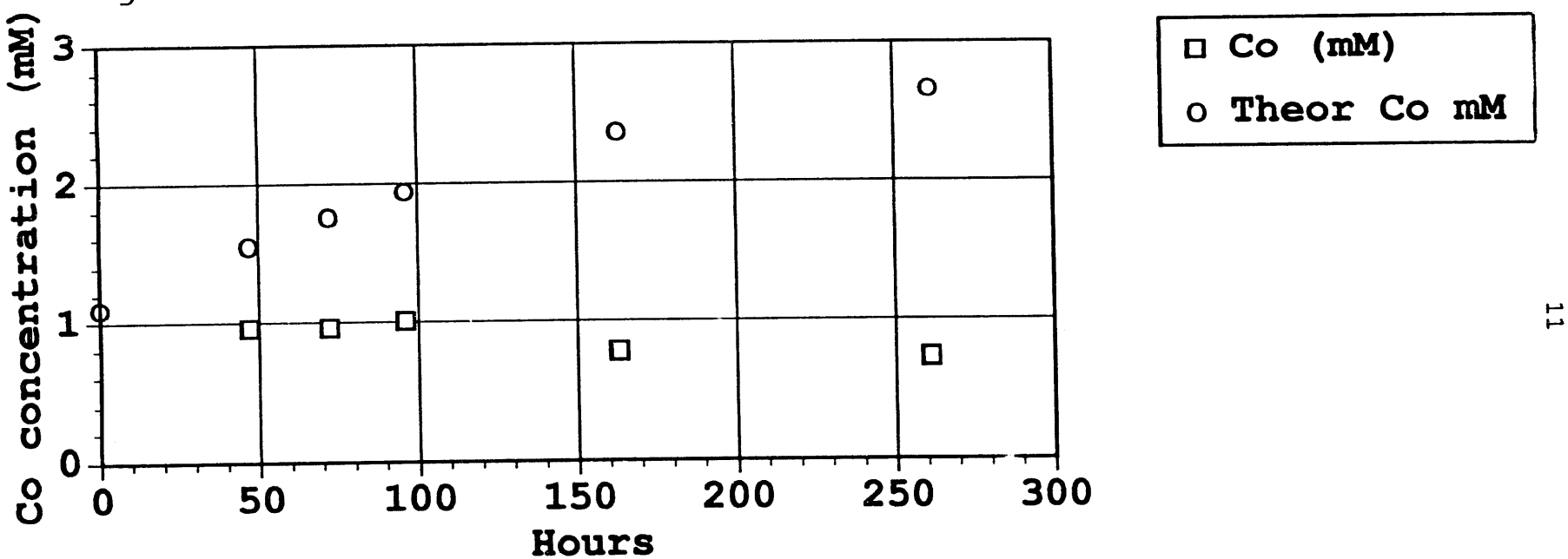


Figure 3. Observed vs. Theoretical Co Concentration



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