Prepared For:

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DRAFT

SCHWARTZWALDER MINE
REFILL WATER REMEDIATION PROJECT

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EXECUTIVE SUMMARY

Cotter Corporation's Schwartzwalder mine is currently filling with water at an estimated rate of 70 gpm. The concentrations of uranium and molybdenum are elevated in the water at average concentrations of 40 and 1.5 mg/L respectively. Cotter Corporation plans to treat the refill water *in situ* and reduce these concentrations to target levels of 59 parts per billion (ppb) uranium and 100 ppb molybdenum so that any water that escapes from the mine working will not degrade adjacent surface water and/or groundwater systems.

This report describes studies conducted by Shepherd Miller to test the feasibility of using bioremediation to treat the mine refill water and lower the concentration of these constituents to target levels. *In situ* bioremediation is a technology that uses microorganisms to reduce, eliminate, or contain contaminants and is applied below-ground at the site of contamination. This is typically accomplished by the addition of specific nutrients that stimulate biological activity. Several bacteria, which are widely distributed in natural systems, have been found to directly reduce uranium and/or molybdenum during anaerobic respiration. In their reduced states, uranium and molybdenum tend to precipitate from solution, forming solids with low solubilities. These reductive processes could therefore be very effective at reducing the aqueous levels of these contaminants and sequestering them within the mine workings.

Pilot scale studies were initiated on October 25, 2001 to test this remedial option. These tests were performed in 30 gallon plastic barrels, which contained mine refill water and waste rock from the mine. Four test systems, which differed in the amount of nutrients added or in the source of the microbial inoculum, were used to evaluate the technology under different conditions.

In general, the effectiveness of the systems with respect to contaminant removal was highly variable. However, one system, was successful at reducing the levels of uranium and molybdenum by 86% and 77% respectively. This bioreactor was amended with a nutrient solution that provided an initial dissolved organic carbon dose of approximately 650 mg/L, and only native microorganisms present either in the mine water or on the wall rock. The

concentration of uranium decreased from an initial level of 45 mg/L to 6.35 mg/l at the end of 12 weeks. During the same period molybdenum levels decreased from 1.9 mg/L to 0.442 mg/L. While these concentrations are still substantially higher than target levels, the duration of the studies is very short when compared to the reaction time that would be available with full-scale treatment (months to years). Thus, the studies were successful as proof of technology for *in situ* biological treatment of the target constituents within the mine.

Details of the methods and results of these investigations are presented in this report.

1.0 INTRODUCTION

This report provides a summary and evaluation of the results of pilot studies performed to test the feasibility of using *in situ* bioremediation for removal of uranium and molybdenum from the Schwartzwalder Mine (SM) refill water. These studies were initiated pursuant to a proposal dated July 26, 2001, submitted to Cotter Corporation by Shepherd Miller.

Section 2.0 provides a brief background of current conditions within the mine and a rationale for testing bioremediation. Section 3.0 explains the methodology employed to test this particular approach. Section 4.0 describes the results of the studies while Section 5.0 provides a discussion of the results with conclusions. Section 6 briefly discusses issues pertinent for scale-up to full-scale treatment.

2.0 BACKGROUND AND RATIONALE

2.1 Project Background

Cotter Corporation's Schwartzwalder Mine is located in the SE ¼ of section 25, T2S, R71W, 6th PM, in northern Jefferson county, Colorado, approximately 8 miles northwest of Golden. The mine is the largest vein type uranium mine in the United States. Initial mining commenced about 1949 after the deposit was discovered by Fred Schwartzwalder on the ridge about 350 feet above Ralston Creek. During mining, water was encountered at several levels, most notably at about 250 feet, and at the 1200, 1600, 1800 and 1900 levels. Consequently, during operations water was continuously pumped from the mine workings.

Pumping of mine water ceased in May 2000 and water is currently entering the mine void space at an estimated 70 gallons per minute (gpm). It has been estimated that, when at capacity, the mine void space will contain approximately 133 million gallons of refill water.

Refill water has been sampled on a monthly basis in the shafts and the exhaust bore hole, at the top pool, and at submerged levels that are accessible. The water has been analyzed for major ions and for several metals including Al, Cu, Fe, Mn, Mo, Sb, and Tl. The constituents that are of primary concern are molybdenum and uranium, which have average concentrations of 1.8 and 45 mg/L respectively in the mine refill water. Consequently, the studies described in this report were initiated to demonstrate the feasibility of using *in situ* bioremediation to reduce the levels of uranium and molybdenum in the Schwartzwalder Mine refill water to target levels of 59 and 100 parts per billion (ppb) respectively.

2.2 Rationale for *In Situ* Bioremediation

Both the uranous (U_4^+) and uranyl (UO_2^{2+}) ions will hydrolyze (react with water) to produce a variety of dissolved solution species. The oxidized uranyl ion (UO_2^{2+}) forms a large number of stable solution complexes with sulfate, phosphate, fluoride, and carbonate. Above a pH of approximately 5, the uranyl ion forms three different soluble complexes with carbonate: the neutral uranyl carbonate species ($UO_2CO_3^0$), a uranyl dicarbonate ion [$UO_2(CO_3)_2^{2-}$], and a uranyl tricarbonate ion [$UO_2(CO_3)_3^{4-}$]. Speciation modeling (USGS PHREEQC) of

Schwartzwalder mine refill water (data provided by Cotter Corp.) suggests that 99.6 percent of the uranium in solution is present as one of these carbonate species. The uranyl carbonate species are largely responsible for the high degree of uranium mobility commonly observed in oxidizing, neutral to high pH ground waters. The uranous ion can also form stable solution complexes. However, solid $UO_{2(s)}$ (uraninite) is also stable under these conditions and is very insoluble. Therefore, under most natural conditions where reducing conditions are prevalent and the uranous ion predominates, solution uranium concentrations are controlled by solid UO_2, which supports a low dissolved U4+ concentration (3 to 30 µg/L). Thus, the reduction of U(VI) to U(IV) with the concomitant precipitation of uraninite can effectively remove uranium form solution.

The direct involvement of microorganisms in the reduction of U(VI) to U(IV) was first demonstrated by Lovley and others in 1991 (Lovley et al., 1991). Several organisms common to soil and subsurface environments have now been identified that can enzymatically reduce U(VI) to U(IV) under anoxic conditions. These include dissimilatory metal-reducing bacteria (DMRB) *Geobacter metallireducens* (Gorby and Lovley, 1992; Lovley et al., 1991), *Shewanella putrefaciens* (Lovley et al., 1991), and *Shewanella alga* strain BrY (Caccavo et al., 1992) as well as sulfate-reducing bacteria (SRB) *Desulfovibrio desulfuricans* (Lovley and Phillips, 1992), *D. vulgaris* (Lovley et al., 1993), and *Desulfotomaculum* reducens sp. nov. strain MI-1 (Tebo and Obraztsova, 1998). Organisms from both groups (i.e., DMRB and SRB) have been shown to obtain energy to support growth via electron transport to U(VI) (Lovley et al., 1991; Tebo and Obraztsova, 1998) as shown in equation [1] in which CH_2O represents organic carbon and presented graphically in Figure 1.

$$2CH_2O + 2UO_2(CO_3)_2^{2-} + 2H_2O \rightarrow 2UO_{2\,(s)} + 5HCO_3^- + H^+ \qquad [1]$$

The geochemistry of molybdenum is similar to that of uranium. Under oxidizing conditions in natural waters, Mo occurs primarily as Mo(VI) and Mo(V) ions HMo_4^{2-}, MoO_4^{2-}, or MoO^{2+}. These ions are highly soluble and mobile in the environment. Under reducing conditions, molybdenum primarily occurs as Mo(IV), forming insoluble phases such as MoS_2, and MoO_2 (Brookins, 1988). The formation of some economically important Mo deposits is thought to be

the result of the chemical reduction of Mo(VI) by sulfide or hydrogen gas in anoxic sedimentary environments. However, the chemical reduction of Mo(VI) by either of these chemical species appears to be slow (Tucker et al., 1997), and others have shown that molybdate in sulfidic solution undergoes sulfidation in four steps that conserve Mo(VI) and lead to the formation tetrathiomolybdate (MoS_4^{2-}), a soluble and mobile species (Erickson and Helz, 2000).

An alternative explanation for the formation of these deposits involves the enzymatic reduction of Mo(VI) by sulfate-reducing bacteria followed by reaction with sulfide to form molybdenite (Tucker et al., 1997) as shown in equation [2].

$$CH_3CHOHCOO^- + 2HmoO_4^- + 4HS^- + 5H^+ \leftrightarrow$$
$$CH_3COO^- + 2\ MoS_{2(s)} + 6\ H_2O + HCO_3^- \qquad [2]$$

Thus in the presence of sulfate, the simultaneous reduction of Mo(VI) to Mo(IV) and SO_4^{2-} to HS^- by SRB leads to the formation of the sparingly soluble solid phase. Under conditions that support the reaction described by equation 2, 99.5 percent of Mo(VI) initially present (~0.1 mg/L) was removed from solution within 13 days and precipitated as MoS_2 (Tucker et al., 1997). In the absence of sulfate Mo is enzymatically reduced by an alternate pathway to an amorphous molybdenum oxide as described by equation [3].

$$CH_3CHOHCOO^- + 2HMoO_4^- + H^+ \leftrightarrow$$
$$CH_3COO^- + 2\ MoO_{2(s)} + 2\ H_2O + HCO_3^- \qquad [3]$$

The reactions shown in equations 1 through 3 thus form the basis for the *in situ* bioremediation technology, which was tested during these pilot scale studies. The mechanism for uranium and molybdenum removal entails the addition of a labile (easily used) organic carbon source to the mine refill water. Native microorganisms couple the oxidation of the organic carbon with the reduction of uranium and molybdenum, thereby causing the *in situ* precipitation of these constituents.

3.0 PILOT SCALE TEST METHODS

3.1 Pilot Study Design and Setup

Approximately 300 gallons of groundwater was collected from the mine on October 16, 2001, and stored in clean, 30-gallon plastic barrels. Pilot-scale studies began on October 25. 2001 as batch reactions in four 30-gallon barrels (Barrels A, B, C, and D described below). Water quality parameters (pH and electrical conductivity) of the stored groundwater were taken in each of the storage barrels prior to mixing and use in reaction barrels.

Wall rock was collected by mine personnel, crushed to cobble size and smaller, homogenized, and stored prior to the initiation of pilot studies. Wall rock was sieved using a standard size ¼ inch sieve, and the coarser fraction (> ¼ inch) was retained. Each reaction barrel was filled with 33.7 pounds of the retained fraction. The waste wall rock was added to approximately simulate the wall rock surface area to volume of water that would be present within the mine. Within each system the wall rock functioned as a site for geochemical reactions, as a potential source for the microbial inoculum, and as an adsorption site for the bacteria. Once rock had been loaded into each barrel they were filled with a homogenous mix of mine-derived groundwater to a volume of approximately 25 gallons. Additional amendments were then added to the following barrels:

Barrel A: 136 ml of a mixture of sugars, short-chain organic acids and alcohol, plus phosphate (henceforth referred to as nutrient solution) to provide a total organic carbon (TOC) loading of 100 mg/L.

Barrel B: 310 ml of the nutrient solution to provide about 650 mg/L TOC

Barrels C: 310 ml of nutrient mixture (~650 mg/L) plus a small inoculum (300 ml) of anoxic soil/sediment, with active anaerobic microbial communities. The additional microbial inoculum was added to one system in case the wall rock and refill water lacked sufficient native organisms to perform the target reaction and thus help to ensure that the requisite populations are activated and the reactions described above would be observed.

Barrels D: No added nutrients, this system served as a qualitative abiotic control.

If refill water does make its way out of the mine, dissolved constituents will then move through porous media that will provide attachment sites and support active microbial populations. Thus, to provide a more accurate assessment of the concentrations of U and Mo that might actually move from the mine through porous media and reach surface water systems, packed columns were added to the design to simulate this movement. Columns were constructed of 4-inch diameter O.D. clear PVC pipe and filled with small diameter pieces of wall rock. An overflow line was fitted into the side of the barrels, approximately 3 inches below the top of the barrels and connected to the columns (see Figure 1 for typical apparatus set-up). Additional groundwater not used in the reaction barrels was stored in separate barrels and was used as feed-water to refill the reaction barrels. Feed-water was pumped with a peristaltic through Teflon® tubing into the bottom of each reaction barrel, allowing inflow water to flow up through wall rock material (Figure 1). The reaction barrels would fill to the level of the overflow line, at which point the water in the reaction barrels would begin to flow into and fill the column. Pump speed was originally set at approximately 3 rpm (0.185 ml/min), a pumping rate to provide a residence time within the columns of about 1-week. The pump speed was adjusted up to 2 rpm (0.37 ml/min) on November 2nd, and pumping new water into the reactors was stopped on December 20th.

3.2 Sampling and Analysis

Sampling: Water samples for field parameters and geochemical analyses were collected at regular intervals during the course of the pilot studies. Field parameter measurements were taken of mine-derived water in the storage barrels prior to initiation of the pilot study to establish initial water quality conditions. Samples from the reaction barrels were collected from depths within the barrels just above the wall rock (see Figure 1 for set-up of sampling ports). Column samples were collected from the effluent end of the columns. Water samples from the barrels were collected at day 4 and at the end of week 2, 3, 4, 5, 9 and 12. Water samples were collected from the columns at the end of 2, 3, 4, 9, and 12 weeks, except when specific columns did not produce sufficient quantities of effluent for analysis. Water samples collected from Barrel F

(feed water) on 10/29/01 are considered to be representative of initial water quality conditions, and were analyzed as the zero time point (t = 0).

Analysis: The aqueous phase was monitored for field parameters temperature, pH, electrical conductivity, and Eh. Laboratory analysis of samples generally included dissolved anions (ammonia, nitrate, sulfate, and sulfide), dissolved cations and trace metals (Fe, Mn, U, Mo), and dissolved organic carbon (DOC). In addition, selected samples (e.g. initial and week 6) were analyzed for a suite of anions and metals (Table 1), plus sulfide and DOC. Energy Laboratories, Inc in Casper, Wyoming performed all analyses.

4.0 PILOT STUDY RESULTS

4.1 Mine Shaft Water Quality

Prior to initiation of the pilot scale studies and while refill water was being collected form the mine, conditions within the mineshaft was measured by lowering an In-Situ® TROLL 8000 down into the mineshaft. The TROLL 8000 simultaneously measures temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP or Eh), and specific conductance. Measurements were taken starting about 65 feet below the 8 Level sill to a depth of 256 feet. Data recorded during this sampling event on October 29, 2001 are presented in Table 2.

Temperature, specific conductance, and pH remained very constant with depth. In contrast, DO decreased with depth from 0.34 to 0.05 mg/L and ORP went from and Eh reading of 154 at the air-water interface to 106 at depth. This suggests that the mine refill water is becoming anoxic with depth and may already be anoxic in the lower levels.

4.2 Water Quality in Primary Bio-Reactors

Water temperature in the barrels dropped over the course of the studies from an average of 16.7 ^{O}C to and average of 13.4 °C (Figure 3). This slight drop in temperature was to be expected considering the seasonal temperature changes but is unlikely to have effected overall reaction rates to any significant degree. Conductivity in Systems A through C rose sharply, when compared to the feed water, after the nutrient solution was added (Figure 4). Specific conductance also rose in reactor D during the studies despite the lack of nutrient addition. It is likely that this was the result of dissolution of wall rock minerals and/or desorption of ionic species from the wall rock as discussed below. It is probable that these reactions between the added wall rock and the refill water also contributed to the rise in conductivity observed in Systems A though C. Solution pH declines in Systems A through C upon the addition of nutrient solution as would be expected with the addition organic acids and the onset of fermentation reactions (Figure 5). At least part of the drop in pH can be attributed to the addition of nutrient solution that consisted of 40% carbohydrate (glucose), 30% organic acids (sodium acetate), and 30% denatured alcohol with and initial pH of 6.1. In addition, as the oxygen in the systems is

consumed the added glucose is fermented to numerous low molecular weight organic acids, such as, lactate, acetate, butyrate and propionate, which will also tend to lower the pH. These fermentation products are then further oxidized to CO_2 during metal and sulfate reduction. Thus, the pH in these barrels began to rise after week 1 primarily as a result of alkalinity produced from anaerobic respiration. The Eh dropped from an initial +187 mV to and average of –206 mV by week 2 in systems to which nutrients were added (Figure 6). Following this initial drop the Eh rose again in these systems until week 4 to an average value of –64 mV after which it again declined to an average of –195 mV. It is difficult to say with any certainty which redox couple is controlling the measured Eh at any given time, however, it is possible that at week 4 the dominant redox couple was Fe^{2+}/Fe^{3+} and by week 12 the dominant couple was most likely SO_4^{2-}/HS^-. This change in the primary redox couple could explain the fluctuations observed in the measured Eh over time. All field measured data from the bioreactor barrels is presented in Table 3.

Uranium levels in all systems dropped by week 2, with the greatest decreases seen in Systems A, B, and C, which dropped from an initial U concentration of 45 mg/L to 31, 33, and 35 mg/L respectively (Figure 7). At least part of the initial decline might be attributed to sorption of the uranyl ion to the walls of plastic barrels. After week 2 the uranium levels in all the systems with the exception of the feed water increased slightly, and from that point each of the test systems operated independently. The concentration of U in System D, which lacked nutrients, generally increased over time from the initial 45 mg/L to 48.4 mg/L at week 12. It is believed that this was due to the leaching of uranium from the wall rock that was added to each reaction vessel. There is no apparent explanation for the dip in U levels at week 5, but it corresponds to a dip in the levels of Mn and Mo and is thought to be a sampling or analytical anomaly. Uranium levels in System A continued to increase until week 9 before decreasing again to a level of 34.8 mg/L at week 12. The concentration of uranium in system C increased only slightly until week 4, declined sharply until week 6 and remained essentially unchanged to week 12. The observed reactivity of uranium seen in System B is more typical of what was expected based on past experience with pilot scale studies and field scale demonstrations of biological mediated uranium reduction. Following the initial drop at week 2, U levels remained fairly constant until week 5 after which they rapidly declined to 6.4 mg/L by week 12, a reduction of about 85 percent.

The concentration of iron increased during the first half of the studies from non-detectable levels to maximum values of 2.6, 6.8, and 3.0 mg/L in Systems A, B, and C respectively (Figure 8). This increase is expected and results from the microbial reduction of iron (hydr)oxides contained in the wall rock. Following week 6 the iron rapidly decreases to near background levels. The decrease in iron levels corresponds to increasing levels of sulfide (see below) and is due to the formation and precipitation of iron sulfide (FeS). In System D, lacking microbial activity, no change in iron levels is observed.

Manganese levels follow a trend similar to that of iron as shown in Figure 9. The concentration of Mn goes from an initial value of 1.9 mg/L to a maximum of 3.7 mg/L in System B, with somewhat lower maximum levels of 3.2 and 2.9 mg/L seen in Systems A and D respectively. Manganese concentrations do not decrease as fast as the iron levels do however, which is to be expected based on the significantly lower rates of manganese sulfide formation. It is not apparent given the current data whether the decrease in Mn levels after week 6 is due to the formation of manganese sulfide or manganese carbonate which can also form in the presence of high alkalinity.

There is a slight increase in the concentration of molybdenum in all systems over the first 2 to 3 weeks as shown in Figure 10. The concentration of Mo continues to increase in System D as molybdenum is leached from the wall rock. In the active biological barrels, Mo levels rapidly decline after week 6 to the final values recorded at week 12 of 0.12, 0.44, and 0.34 in barrels A, B, and C respectively. This decline also correlates to increasing levels of sulfide and is likely the result of the formation and precipitation of MoS.

Sulfide levels begin to rise in all biologically active systems by week 5 (Figure 11) and continue to rise until week 12 in Systems A and C to levels of 28 and 40 mg/L respectively. It is unclear why after increasing until week 9 in system B sulfide levels then sharply decline by week 12. This may be due to the initially high levels of iron observed in System B and the removal of sulfide via the formation of FeS. It is also possible that at least a portion of the sulfate-reducing bacteria in System B switched to uranium as the primary electron acceptor in stead of sulfate as these organisms have been shown to use both substrates in respiration.

The levels of DOC generally decline continuously over the course of the studies as would be expected given the consumption of the added organic compounds in microbial respiration (Figure 12). The decline in DOC in Systems B and C is however considerably more rapid during the first 4 to 5 weeks as compared to the last 6 weeks of the study. This is probably the result of rapid population growth in the initial few weeks and the incorporation of organic carbon into cellular mass.

4.3 Water Quality in Overflow Columns

Results from the overflow columns, which were to function as a secondary reaction chamber, did not provide much useful or relevant data. In addition, due to uneven flow rates to each of the barrels coupled with problems associated with the clogging of tubing, it was often not possible to get a sample from the columns for analysis. However, the primary difficulty in interpreting the data results from the use of waste wall rock as the solid phase matrix. There were significant increases in almost every analyte as water from the barrels passed through the columns. As an example, in Column B, the nitrate concentration went from non-detectable in the barrel to 710 mg/L in the column effluent, sulfate went from about 2000 mg/L to 9900 mg/L, uranium went from 33 mg/L to 145 mg/L, and other constituents had substantial increases as well. It became apparent that the waste wall rock was not the appropriate material to employ in the secondary reaction vessel, and the implications are discussed in the following section.

4.4 Headspace Air Quality

Once the smell of sulfide could be detected during sampling, the headspace of the reactors was sampled for gaseous hydrogen sulfide. A hydrogen sulfide concentration of 35 ppm was recorded for the air sample taken from System B at 12 weeks. This was the only sample taken that was above the detection limit of 2 ppm. While this may not be representative of concentrations that would be seen in mine void space during treatment it should be noted that this concentration is above the OSHA ceiling of 20 ppm.

5.0 RESULTS: DISCUSSION AND CONCLUSIONS

Overall the results from the pilot scale studies designed to test the feasibility of using bioremediation as a means of removing uranium and molybdenum from Schwartzwalder Mine refill water were ambiguous. However, despite this ambiguity, there is indication that this technology may be a practical remedial alternative.

Molybdenum was reduced to near the target level of 100 ppb in all systems to which nutrients were added (Figure 10). In addition, from week 6 to week 12 the uranium concentration in System B, containing only native microorganisms and an initial nutrient addition to supply 650 mg/L DOC, declined about five fold from 30.1 mg/L to 6.35 mg/L (Figure 7). While this uranium concentration is still considerably higher than the target level of 0.059 mg/L, with continued reaction time the reduction of uranium to target level may be achieved.

The ambiguity in the results comes from the less than predicted reduction of uranium, and the difference in reduction trends seen in the other two nutrient amended systems. System A was amended with a nutrient solution to provide approximately 100 mg/L DOC and contained only native microorganisms supplied in the mine refill water or attached to the added wall rock. System C was amended with a level of organic carbon equivalent to that in System B but also was inoculated with an anaerobic sediment slurry containing organisms preconditioned with nutrients and mine water. The key with respect to the amount of uranium reduction seen in these systems appears to depend on which microbial populations dominated the reactions. While it is tenuous to attempt to accurately describe microbial population dynamics without having quantified any organisms, some indication of what is happening in a system can be predicted based on observed geochemical reactions.

From the geochemical data, it appears that dissimilatory-metal reducing bacteria were a more prominent part of the microbial ecology in System B than in the other two nutrient amended systems. This is suggested by the greater release of both iron and manganese observed in System B as compared to Systems A and C (Figures 8 and 9). The level of iron seen in Reactor B at week 5 was more than 2 times higher than the level observed in the other biologically active

systems (Figure 8). In addition, the level of sulfate reduction, as measured by sulfide production, appears to decrease in Reactor B between week 9 and 12 while the uranium level continued to decrease. In contrast, in Reactors A and C, sulfide continued to increase while the level of uranium either decreased slowly (Reactor A) or increased slightly (Reactor C, Figure 7). Thus, the data suggest that there was a dynamic balance between metal and sulfate reduction in System B, whereas the other biologically active systems appeared to be dominated by sulfate reduction.

Implementation at the field scale should enhance the likely hood that dissimilatory metal and sulfate reduction is more in balance. In theory, which is supported by what has been observed in many natural systems, metal reduction will precede sulfate reduction due to the greater energy released by reduction of most metals when compared to sulfate. In pilot scale studies, the relatively small size of the reactors and consequently the small amount of material incorporated into the reactors can tend to selectively favor specific populations over others. Within the mine it is likely that a much more diverse microbial consortium will be present. Further, due to the low nutrient conditions now present in the mine workings, the greater energy yield from metal reduction should favor the survival and growth of dissimilatory metal reducing bacteria over sulfate-reducing bacteria. Thus, current conditions within the mine may be providing and *in situ* selection mechanism favoring the target metal-reducing organisms.

Columns were added into the pilot scale studies to simulate reactions that may take place once mine refill water escaped from the mine and migrated through geological material. In theory, the greater surface area to volume would provide additional attachment sites for bacteria and should enhance local microbial activity and provide a zone for further metal reduction. The columns did not prove to function in this manner due to the large amount of metals and anions that were leached from the added waste rock. It is assumed that much of the leaching associated with the waste rock is due to it having been exposed to unsaturated, oxidizing conditions prior to being used in these studies. The rapid increase on sulfate, nitrate and other constituents suggests that this material was coated with easily solubilized salts. It is unlikely that the native, undisturbed geological material would exhibit the same reactivity and therefore should actually provide a secondary reaction zone that would favor further metal and sulfate reduction.

In summary, while the pilot studies that were run for a period of 12 weeks provided inconclusive results, one study system containing approximately 600 mg/L dissolve organic carbon and native microorganisms provided evidence that bioremediation could be effective for removing uranium and molybdenum from Schwartzwalder Mine refill water. The inconsistency of the results from one system to another highlights the fact that natural systems tend to be very complicated geochemically and microbiologically. However, many of the limitations that are inherent in any pilot study, such as, small size, the use of non-representative material, and relatively short reaction times are overcome in the field. Continuation of the present tests may provide additional insight into the effectiveness of this treatment technology.

6.0 SCALE-UP ISSUES

Unit quantity of materials required: Based on the results of the pilot studies, a recommended target level for dissolved organic carbon in the mine is 350 mg/L. In the initial proposal a concentration of 100 mg/L TOC was calculated to be sufficient to remove uranium and molybdenum to target levels based on refill water chemistry and published reaction stoichiometry. However, this was also based on metals consuming all the electron equivalents prior to the induction of sulfate reduction. It is obvious from the pilot studies that metal reduction and sulfate reduction will likely proceed simultaneously. The 100 mg/L supplied to System A appeared to be insufficient to remove uranium and molybdenum to target levels given the level of sulfate reduction observed in this system. The higher dosage (~650 mg/L) supplied to Systems B and C would appear to be somewhat in excess as there is still almost 300 mg/L available in System B at the end of 12 weeks.

A total organic carbon loading of 350 mg/L translates to approximately 7.8×10^5 lbs. of an organic carbon mixture of sugars, alcohol, and short-chained organic acids and phosphate. This quantity is based on treatment of 133 million gallons, the total volume of water projected to occupy the mine workings when full. It should be noted that this would not all be added at once but would be added over time to maintain a level of DOC between about 250 to 400 mg/L. Costs associated with delivery and application of the nutrient material will depend on the exact mixture of organic carbon compounds, the current market price of the materials, and the delivery destination. It should also be noted that numerous patents currently exist that cover a variety of remedial approaches designed to remove heavy metals and radionuclides from waste water and groundwater systems. It is the responsibility of Cotter Corporation to determine the applicability of such patents to the treatment of the Schwartzwalder Mine.

Delivery of treatment: Biological treatment of mine refill water requires the introduction of a labile and soluble organic carbon and other trace nutrients. Therefore delivery of reactant to the mine workings will be straightforward and should present no major challenge. The introduction of carbon compounds with different densities will enhance mixing within the mineshaft and should facilitate the transition to uniformly reducing conditions. This is of considerable importance when considering the delivery of reductant to a mine, which is already filled to about

half its total capacity. This being said, enhancement of delivery and mixing via installation of delivery conduits and pumping capabilities for water recirculation prior to mine filling would condense the time required to get thorough mixing and thereby decrease the time required to remove the constituents of concern from the aqueous phase.

Conceptually this would entail providing a delivery conduit such that the nutrient solution could be delivered though the exhaust bore-hole and mine water could be re-circulated by pumping from shafts 2 and/or 3 and re-injected via the piping to the exhaust bore-hole, or vice versa. Additionally, nutrient solution would also be delivered via the existing 10 to 12-inch conduit that is already in place and which extends to level 12, which would allow for a 2-point injection system to enhance mixing. Rough calculations based on re-circulating approximately 133 million gallons of water, the projected capacity of the mine workings, indicate that it would require approximately 2 months to re-circulate that volume of water using an 8-inch diameter pipe. Therefore, if installation of pumping and delivery infrastructure is being considered, we would recommend installation of pipe with a minimum diameter of 8 inches.

The above discussion of engineering needs for delivery of a nutrient solution to the Schwartzwalder Mine workings is conceptual in nature. As was suggested in our meeting with Cotter personnel prior to initiation of these pilot studies, finalization of a delivery system will likely require a meeting of Cotter staff familiar with the mine and Shepherd Miller engineers. If bioremediation of the Schwartzwalder Mine proves to be the best alternative based on the results of pilot studies and cost/maintenance considerations, a meeting of Cotter personnel familiar with the mine working and Shepherd Miller engineers will be scheduled so that a final delivery design can be determined.

Long term maintenance: One of the greatest advantages of the proposed remedial approach is the low long term maintenance costs typically associated with the technology. Maintenance may include addition of a limited quantity of nutrients to the mine to maintain reducing conditions and continued monitoring of refill water.

The exact quantity of nutrients that will be required to maintain reducing conditions and keep the concentrations of U and Mo low will be determined by the rate at which oxidants (e.g. O_2, NO_3^-

etc.) diffuse into the mine. Based on the minimal amount of water surface area that is exposed to the atmosphere compared to the large total volume of water entrained in the mine it is estimated that the amount of nutrients required to preserve low levels of the target elements will be very low. In addition, sulfide minerals produced and precipitated during the treatment process should act to provide a buffer to changes in redox conditions.

TABLES

Table 1. Long List of Analytes Measured Prior to Bioreactor Set Up and Again at Week Six

Analyte	Units	Initial Sampling 10/16/01	System A 12/06/01	System B 12/06/01	System C 12/06/01	System D 12/06/01
Aluminum	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1
Arsenic	mg/L	0.003	0.005	0.003	0.005	0.008
Barium	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	mg/L	0.36	0.4	0.4	0.4	0.4
Cadmium	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005
Calcium	mg/L	320	399	433	402	386
Chloride	mg/L	29.4	41	43	42	46
Chromium	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05
Copper	mg/L	<0.01	0.02	0.01	0.03	0.05
Iron	mg/L	<0.03	1.89	3.42	1.62	<0.03
Lead	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05
Magnesium	mg/L	230	304	293	299	319
Manganese	mg/L	1.5	3.20	3.02	2.86	1.91
Mercury	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001
Molybdenum	mg/L	1.9	1.3	1.9	1.3	2.8
Nickel	mg/L	<0.05	<0.05	0.06	<0.05	0.06
Potassium	mg/L	18.5	27	23	23	21
Radium 226	pCi/L		136	85.0	88.9	158
Selenium	mg/L	0.002	<0.001	0.001	0.001	0.010
Silica	mg/L	9.4	12.0	11.4	10.8	9.63
Sodium	mg/L	206	252	306	306	216
Sulfate	mg/L	1570	2000	2140	2170	2080
Uranium	mg/L	43	38	30	28	43
Vanadium	mg/L	0.11	<0.1	<0.1	<0.1	<0.1
Zinc	mg/L	0.34	<0.01	0.01	0.01	0.39
A/C Balance (± 5)	%	4.51	5.09	3.16	2.31	4.06
Alkalinity, Total as CaCO3	mg/L	356	501	586	548	363
Anions	meq/L	40.8	52.8	57.6	57.4	53.0
Bicarbonate as HCO3	mg/L	434	611	714	668	443
Carbonate as CO3	mg/L	<1	<1	<1	<1	<1
Cations	meq/L	44.6	58.5	61.3	60.2	57.4
Fluoride	mg/L		1.2	1.2	1.2	1.2
pH	s.u.	7.60	7.70	7.00	7.20	8.1
Solids, Total Dissolved Calculated	mg/L		3375	3640	3619	3409
Nitrogen, Ammonia as N	mg/L	0.07	0.28	0.13	0.18	0.29
Nitrogen, Nitrate+Nitrite as N	mg/L	1.4	<0.05	<0.05	<0.05	13.2
Sulfide	mg/L	<1	3	<1	4	<1
Organic Carbon, Dissolved (DOC)	mg/L	3.43	69	353	331	3.0

Table 3. Field Measured Parameters Taken from Bioreactor Barrels

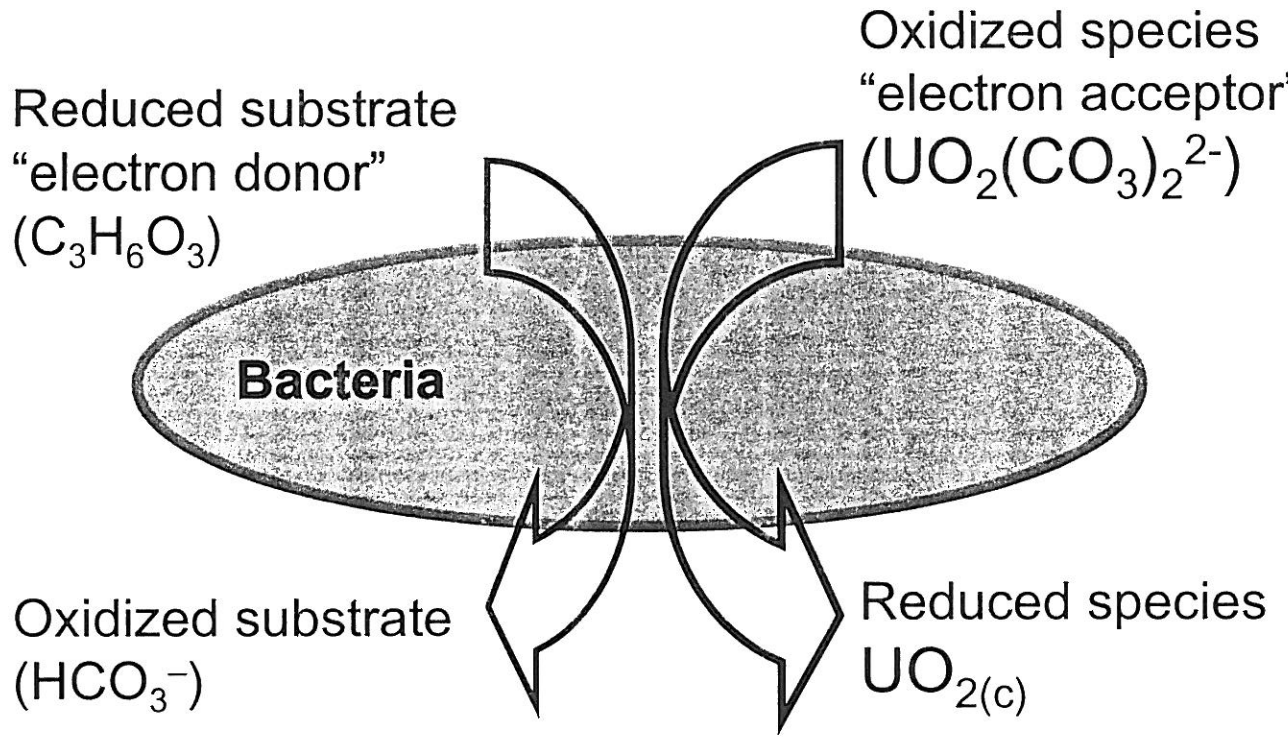
Date	Time Pt.	Syst. A	Syst. B	Syst. C	Syst. D	Feed solu.
pH						
10/25/01	0	7.29	7.29	7.29	7.29	7.29
10/29/01	0.5	6.75	7.48	6.42	7.39	7.60
11/08/01	1	6.69	6.16	6.19	7.46	7.88
11/15/01	2	6.82	6.33	6.20	7.53	8.12
11/21/01	3	7.03	6.16	6.48	7.45	7.81
11/29/01	4	7.03	6.60	6.58	7.47	8.10
12/06/01	5	7.06	6.4	6.5	7.55	
12/13/01	6	7.13	6.62	6.73	7.8	
12/27/01	9	7.22	6.64	6.84	7.58	
01/17/01	12	7.33	6.77	7.16	7.57	
Eh						
10/25/01	0	187	187	187	187	187
10/29/01	0.5					
11/08/01	1	54	-5	30	49	140
11/15/01	2	-168	-174	-275	21	48
11/21/01	3	-75	-182	-72	-2	
11/29/01	4	-89	-58	-46	0	29
12/06/01	5	-109	-88	-83	7	
12/13/01	6	-141	-93	-123	-67	
12/27/01	9	-160	-127	-123	2	
01/17/01	12	-193	-175	-215	-0.92	
Conductivity						
10/25/01	0	3.39	3.39	3.39	3.39	3.39
10/29/01	0.5	3.66	3.69	3.76	3.54	3.37
11/08/01	1	3.79	3.9	3.96	3.57	3.45
11/15/01	2	3.76	3.92	4.03	3.54	3.33
11/21/01	3	4.07	4.16	4.09	3.88	3.35
11/29/01	4	3.72	4.22	3.90	3.66	3.32
12/06/01	5	3.85	4.08	4.06	3.77	
12/13/01	6	3.74	3.95	4.02	3.51	
12/27/01	9	3.64	3.94	3.93	3.63	
Temperature						
10/29/01	0.5	16.7	16.8	16.6	16.8	16.5
11/08/01	1	16.9	17	16.3	16.6	15.6
11/15/01	2	15.4	15.2	14.8	14.2	15.3
11/21/01	3	15.7	15	14.8	14.7	14.9
11/29/01	4	13.1	12.3	11.8	12.7	12.3
12/06/01	5	15.0	14.4	14.2	14.2	
12/13/01	6	14.1	14.3	13.5	13.8	
12/27/01	9	13.9	13.7	13.2	13.3	
01/17/01	12	13.5	13.6	13.6	12.9	

Table 5. Field Measured Parameters from Over-flow Columns

Date	Time Pt. (wks)	Column A	Column B	Column C	Column D
pH					
10/25/01	0				
10/29/01	0.5				
11/08/01	1				
11/15/01	2	7.33	7.16	7.09	7.20
11/21/01	3	7.13			7.24
11/29/01	4	7.05	6.90	6.81	7.25
12/06/01	5	7.09	7.17		7.36
12/13/01	6				
12/27/01	9				
01/17/01	12	7.15			7.40
Eh					
10/25/01	0				
10/29/01	0.5				
11/08/01	1				
11/15/01	2	74	123	147	152
11/21/01	3	-50			28
11/29/01	4	-93	15	15	57
12/06/01	5	-113	-88		3
12/13/01	6				
12/27/01	9				
01/17/01	12	-106			
Conductivity					
10/25/01	0				
10/29/01	0.5				
11/08/01	1				
11/15/01	2	8.85	12.2	12.2	10.11
11/21/01	3	4.52			5.92
11/29/01	4	4.84	4.69	4.31	4.76
12/06/01	5	4.52	5.18		4.47
12/13/01	6				
12/27/01	9				
01/17/01	12				
Temperature					
10/29/01	0.5				
11/08/01	1				
11/15/01	2	15.5	15.3	14.8	14.2
11/21/01	3	15.1			14.2
11/29/01	4	12.5	13.3	12.1	11.7
12/06/01	5	14.0	13.9		13.3
12/13/01	6				
12/27/01	9				
01/17/01	12	12.6			11.7

Table 6 Analytical Results of Over-flow Column Effluent

DATE	Fe (mg/L)	Mn (mg/L)	Mo (mg/L)	SO4 (mg/L)	U(nat) (mg/L)	HS- (mg/L)	NH3 (mg/L)	NO3 (mg/L)	DOC (mg/L)
A column									
25-Oct-01									
08-Nov-01	<0.03	4.74	5.9	6900	84		4.1	283	401
15-Nov-01	<0.03	3.75	5.1	5240	84		1.24	101	195
29-Nov-01	15.7	7.41	1.67		29.2	<1			
17-Jan-02	19.4	6.56	2.89		42.7	<1.0			9.2636
B column									
25-Oct-01									
08-Nov-01	<0.03	4.73	7.4	9920	145		6.0	710	542
15-Nov-01	<0.03	3.38	5.0	5380	104		1.80	92.0	
29-Nov-01	0.222	3.33	2.41		58.9	<1			
17-Jan-02									
C column									
25-Oct-01									
15-Nov-01	<0.03	2.82	2.8	4040	56		1.89	147	445
29-Nov-01	0.0746	2.52	1.5		36.2	<1			
17-Jan-02									
D column									
25-Oct-01									
15-Nov-01	<0.03	3.35	4.4	5590	80		4.08	221	213
29-Nov-01	<0.03	1.73	2.63		51.5	<1			
17-Jan-02	**<0.03**	2.64	3.18		68.1				8.6512



$$6UO_2(CO_3)_2^{2-} + C_3H_6O_3 + 6H_2O \rightarrow 6UO_{2(c)} + 15HCO_3^- + 3H^+ \quad \Delta G^0 = -5446 \text{ kcal/mole}$$

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FIGURE 1
SIMPLIFIED DIAGRAM OF ANAEROBIC RESPIRATION SHOWING THE OXIDATION OF LACTATE WITH THE REDUCTION OF URANIUM

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Project:	P:\100844
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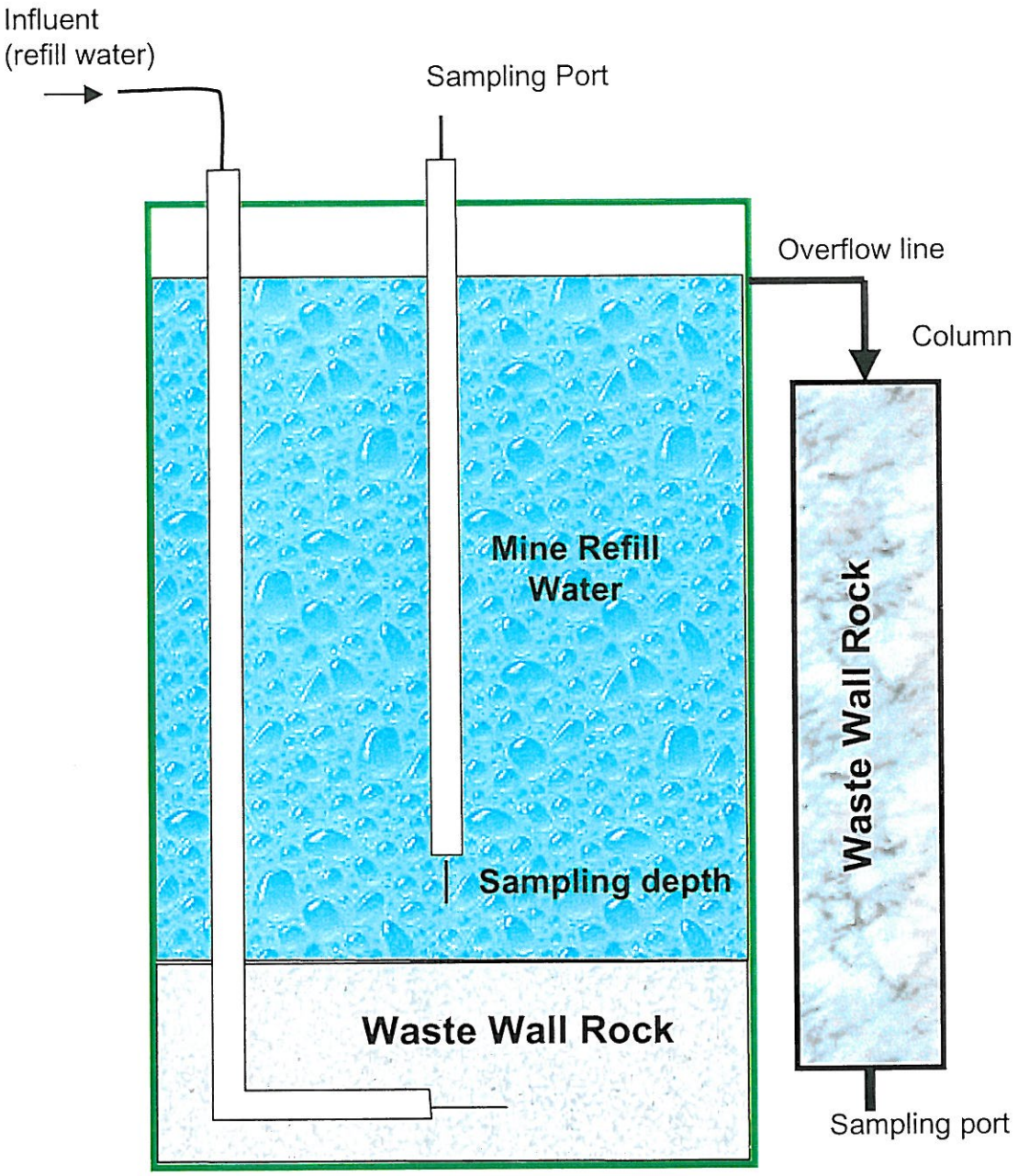

SHEPHERD MILLER INCORPORATED	FIGURE 2 SIMPLIFIED DIAGRAM OF BIOREACTOR SETUP	Date: FEBRUARY 2002 Project: P:\100844 File: PILOT STUDY FIG 2.ppt

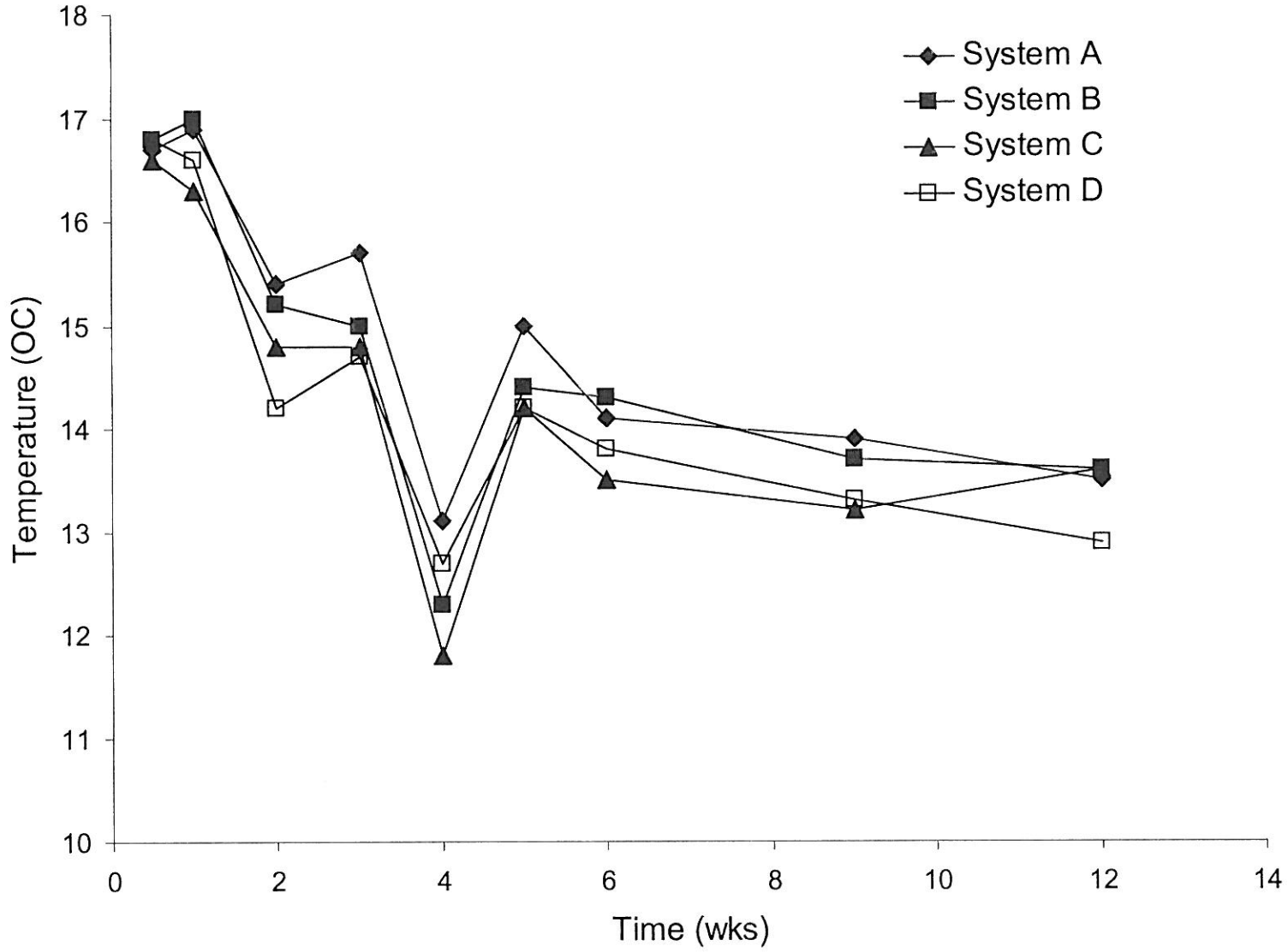

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FIGURE 3
REFILL WATER TEMPERATURE IN BIOREACTOR BARRELS AS A FUNCTION OF TIME

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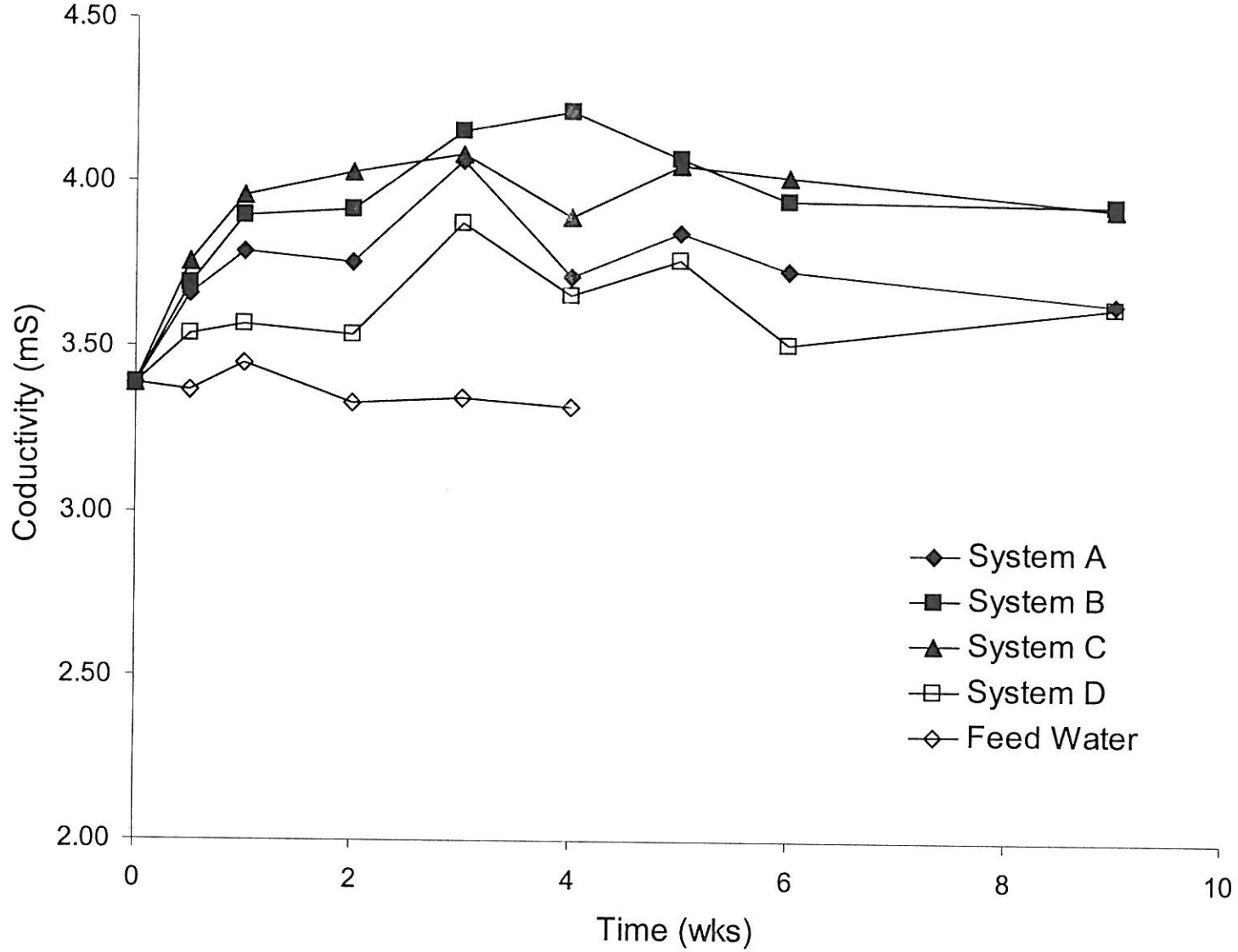

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FIGURE 4
SPECIFIC CONDUCTIVITY MEASURED IN BIOREACTOR BARRELS AS A FUNCTION OF TIME

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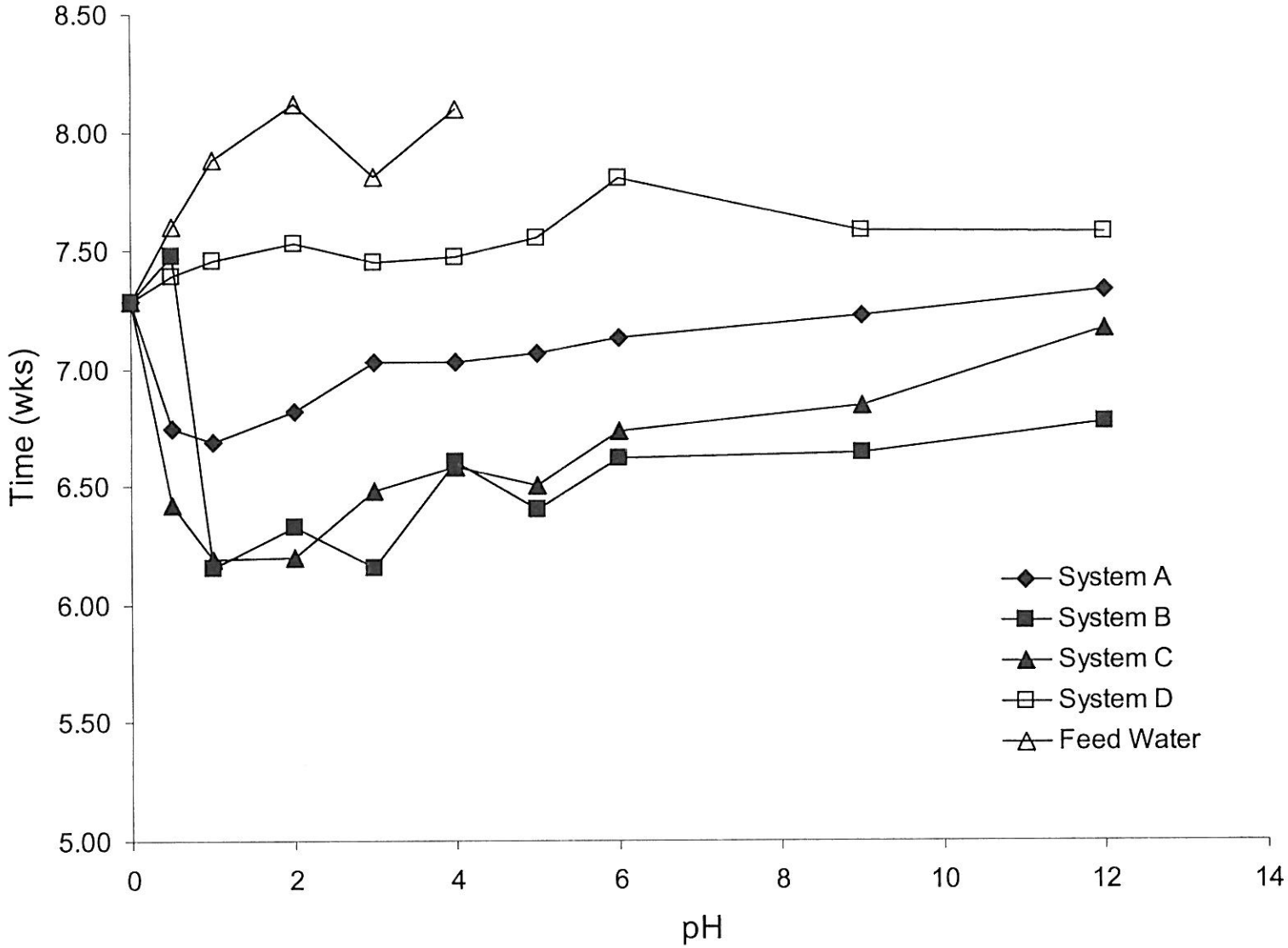

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FIGURE 5
MEASURED pH IN BIOREACTOR BARRELS AS A FUNCTION OF TIIME

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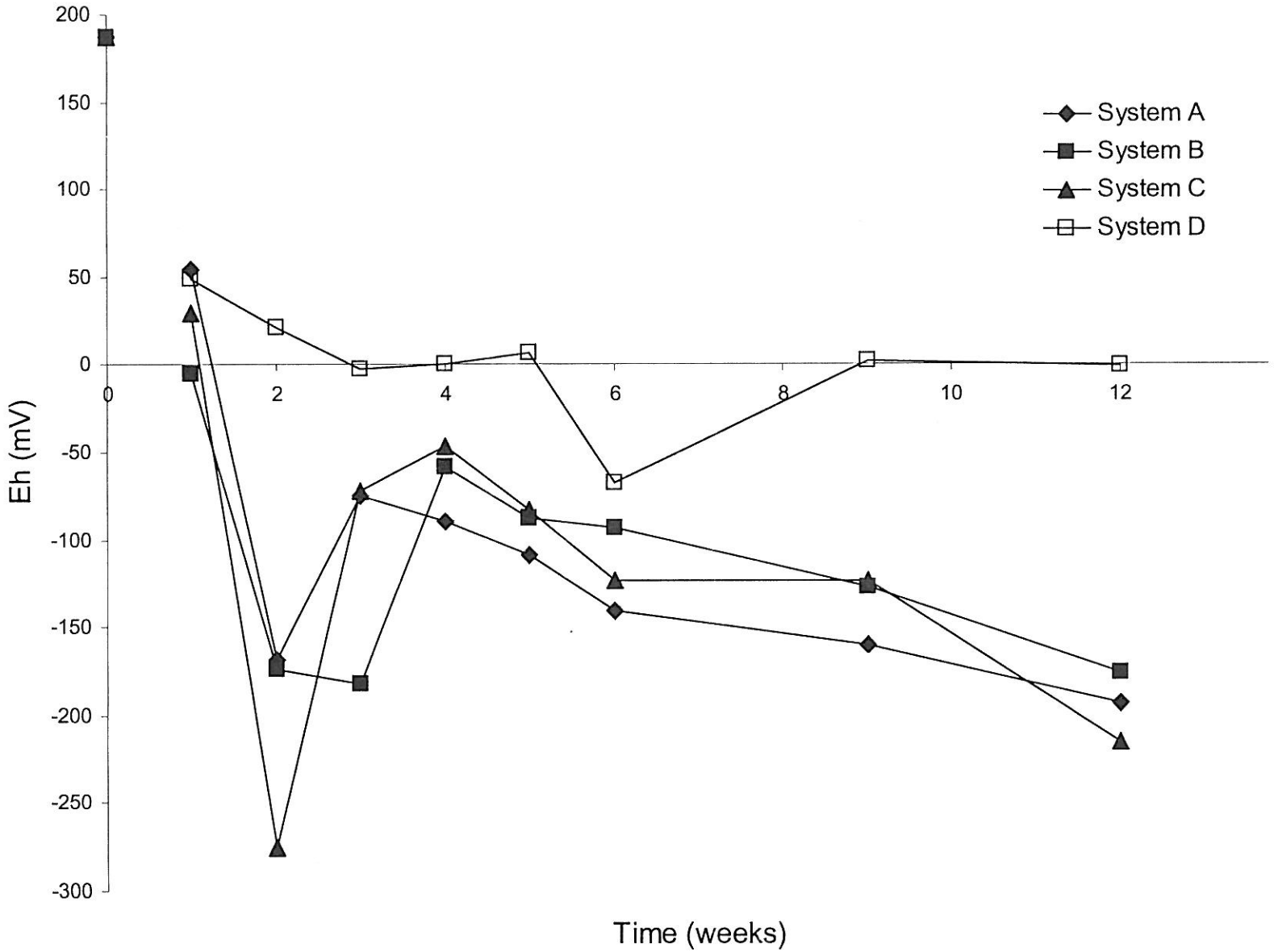

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FIGURE 6
MEASURED OXIDATION-REDUCTION POTENTIAL (Eh) IN BIOREACTOR BARRELS AS A FUNCTION OF TIME

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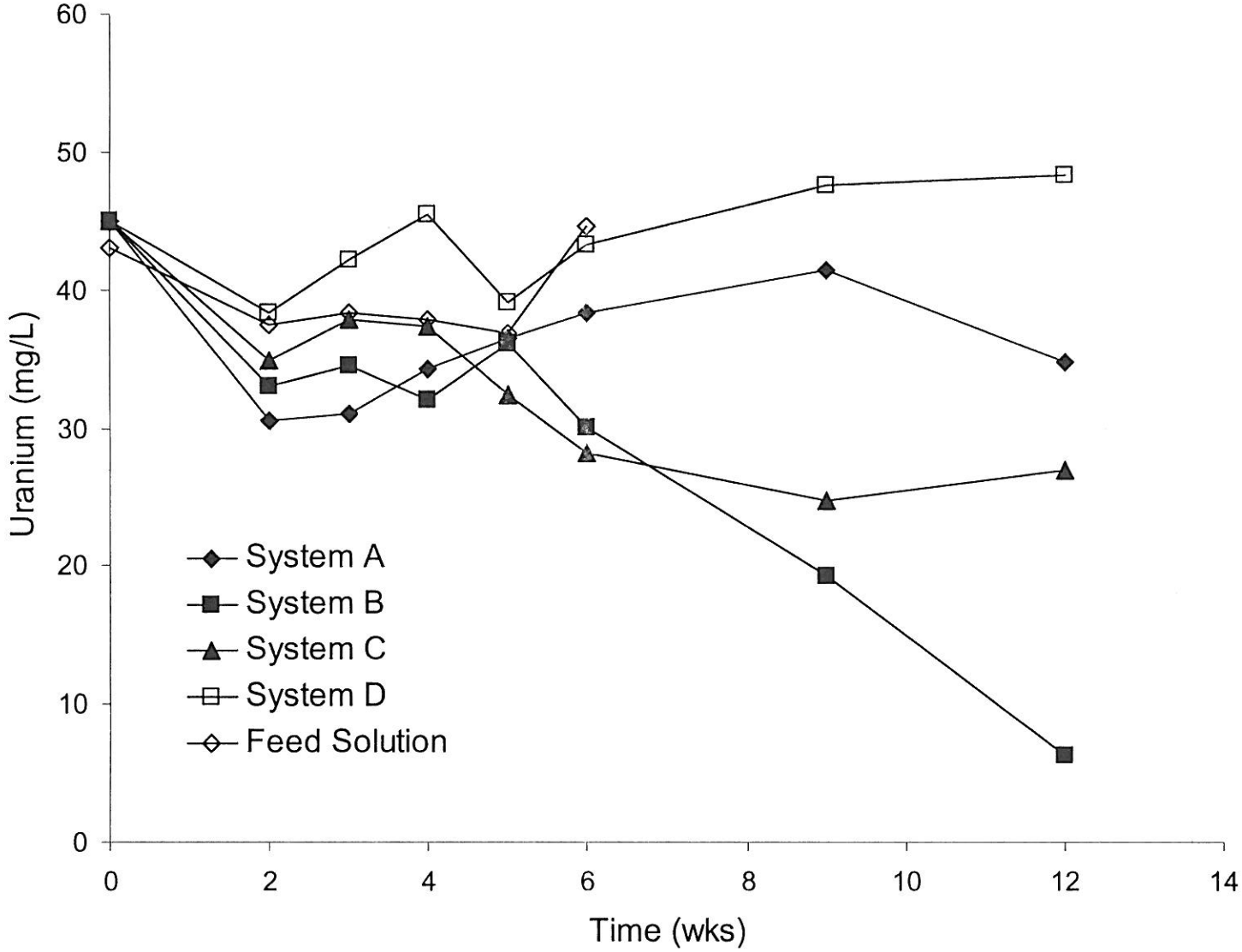

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FIGURE 7
URANIUM CONCENTRATION AS A FUNCTION OF TIME MEASURED IN BIOREACTOR BARRELS

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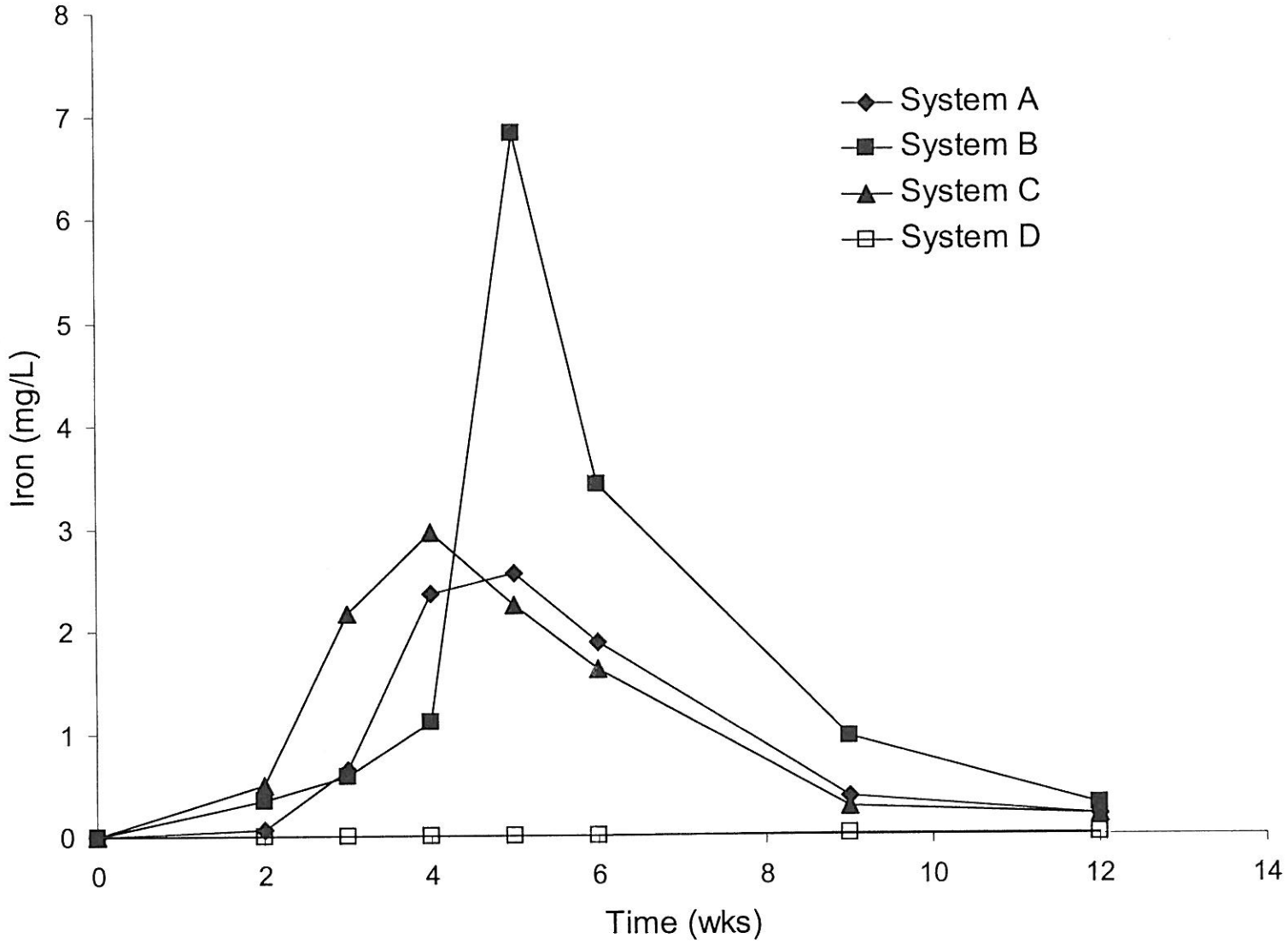

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FIGURE 8
CONCENTRATION OF IRON AS A FUNCTION OF TIME MEASURED IN BIOREACTOR BARRELS

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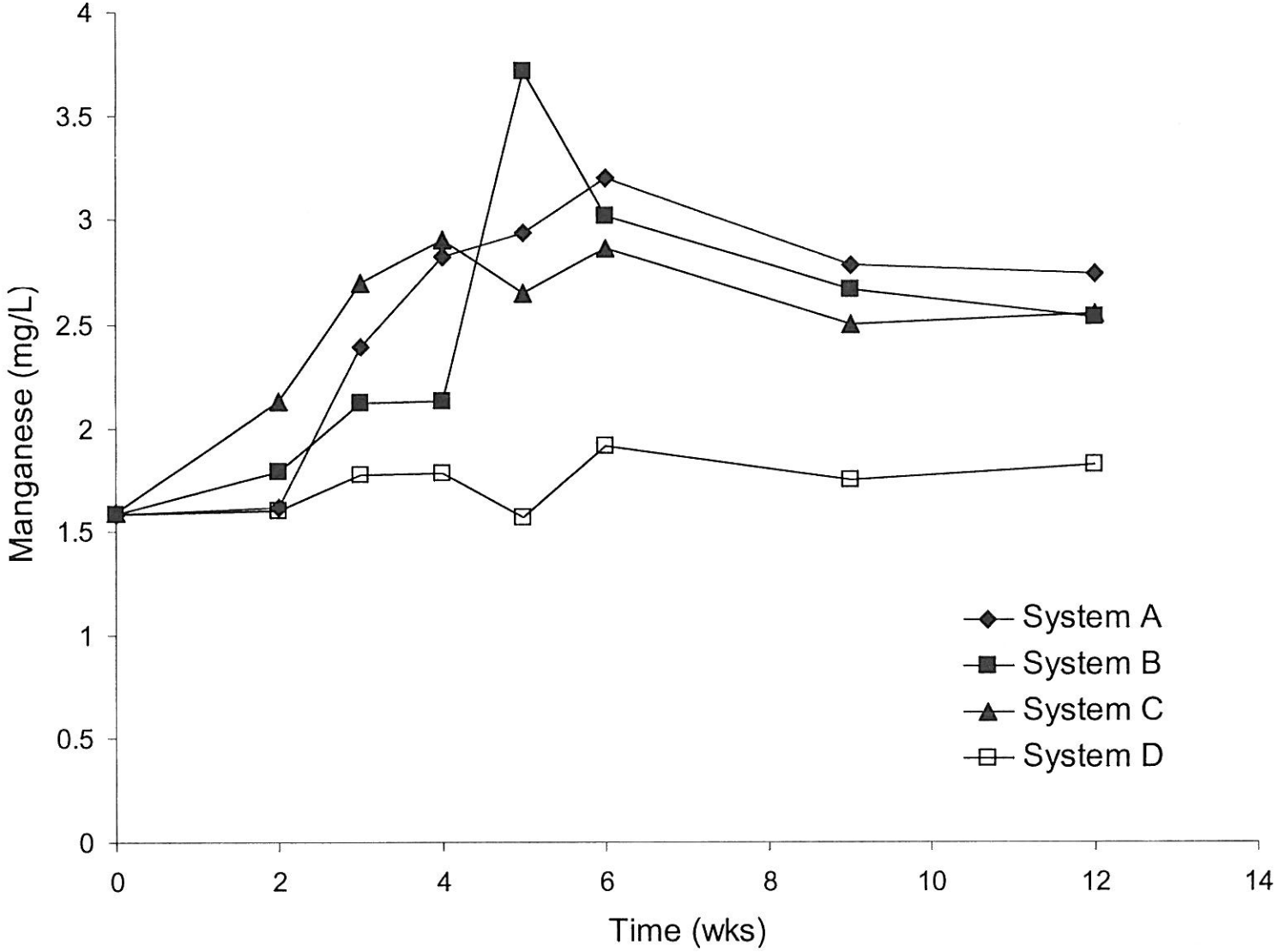

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FIGURE 9
CONCENTRATION OF MANGANESE AS A FUNCTION OF TIME
MEASURED IN BIOREACTOR BARRELS

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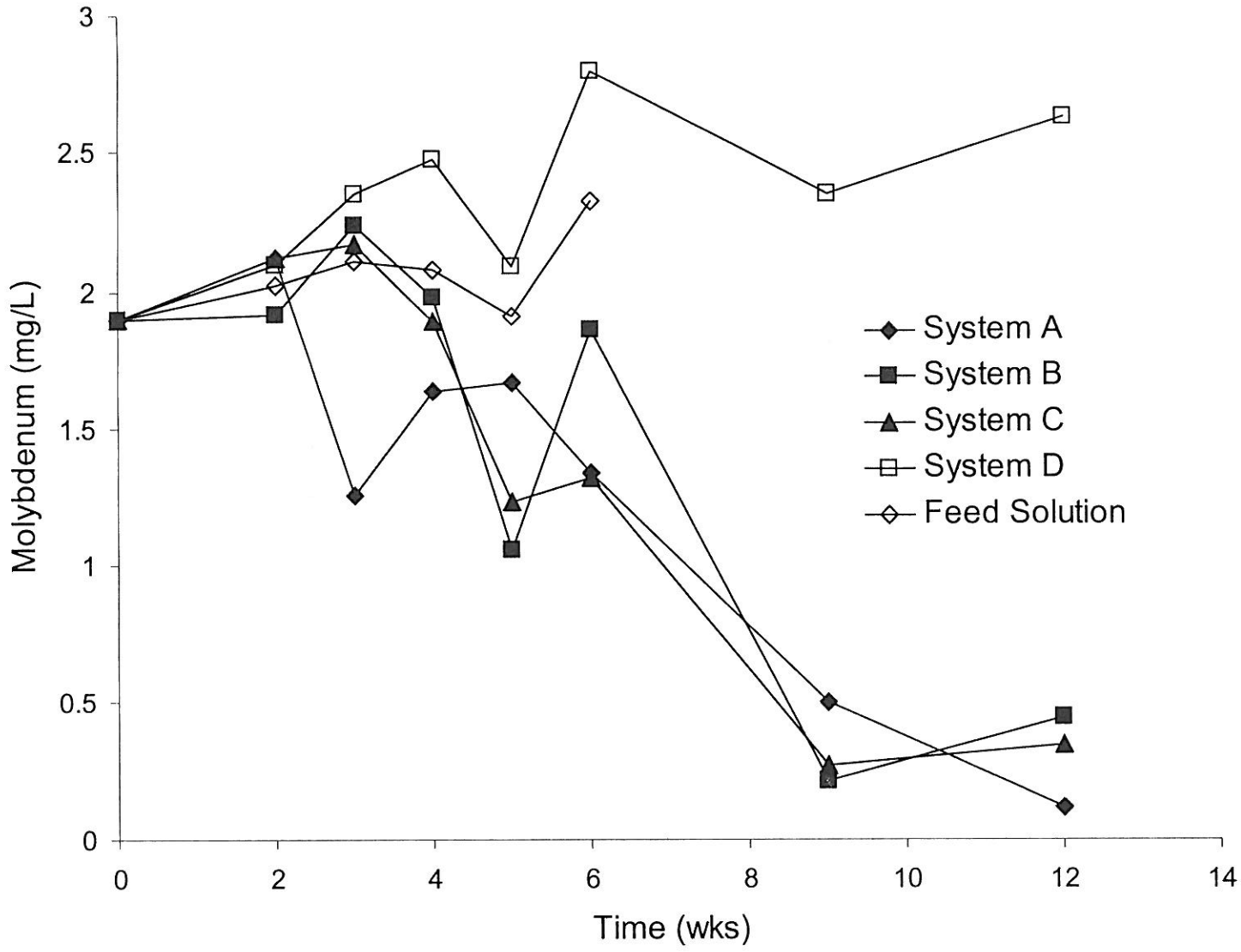

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FIGURE 10
CONCENTRATION OF MOLYBDENUM AS A FUNCTION OF TIME
MEASURED IN BIOREACTOR BARRELS

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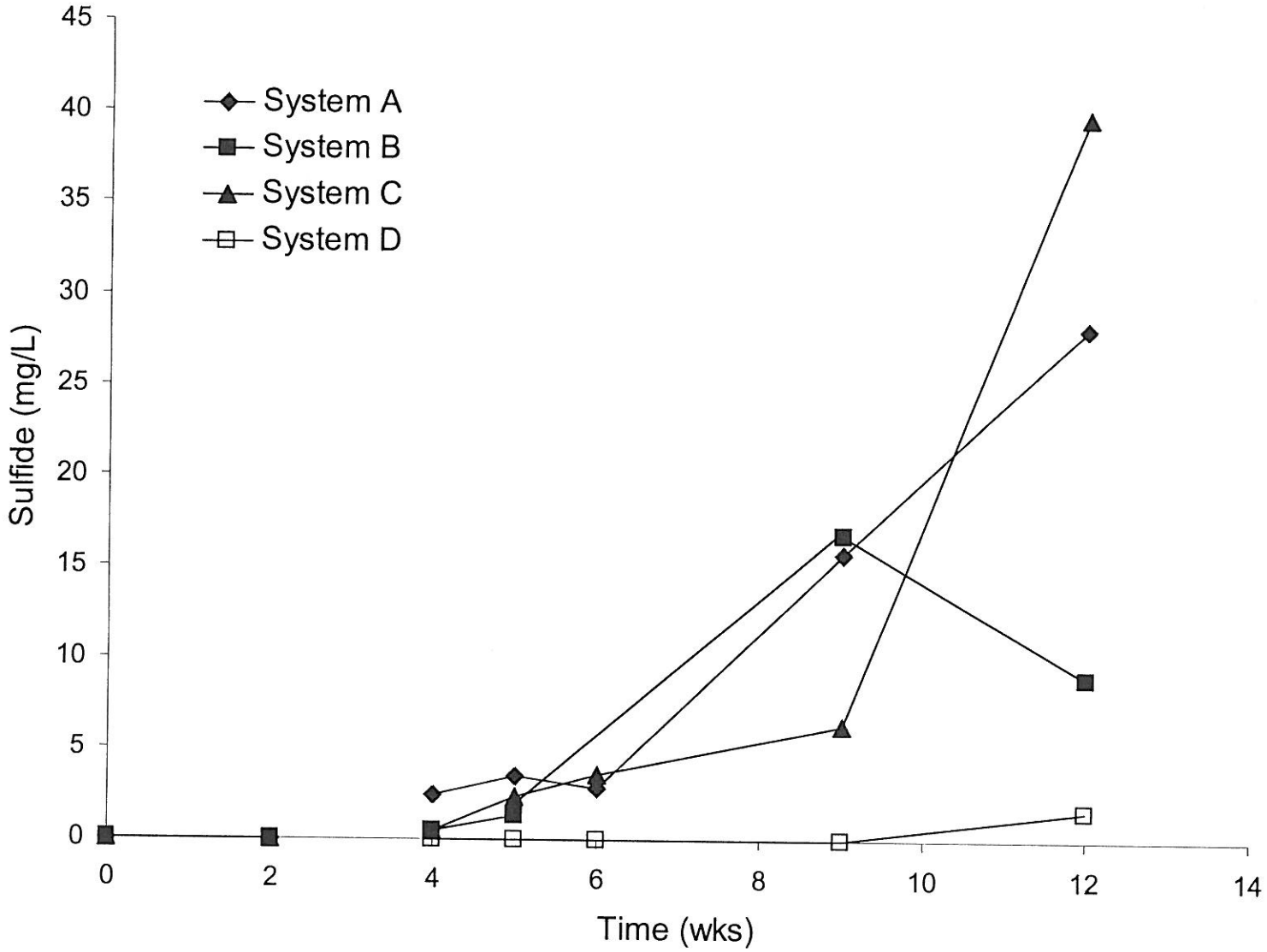

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FIGURE 11
CONCENTRATION OF SULFIDE AS A FUNCTION OF TIME MEASURED IN BIOREACTOR BARRELS

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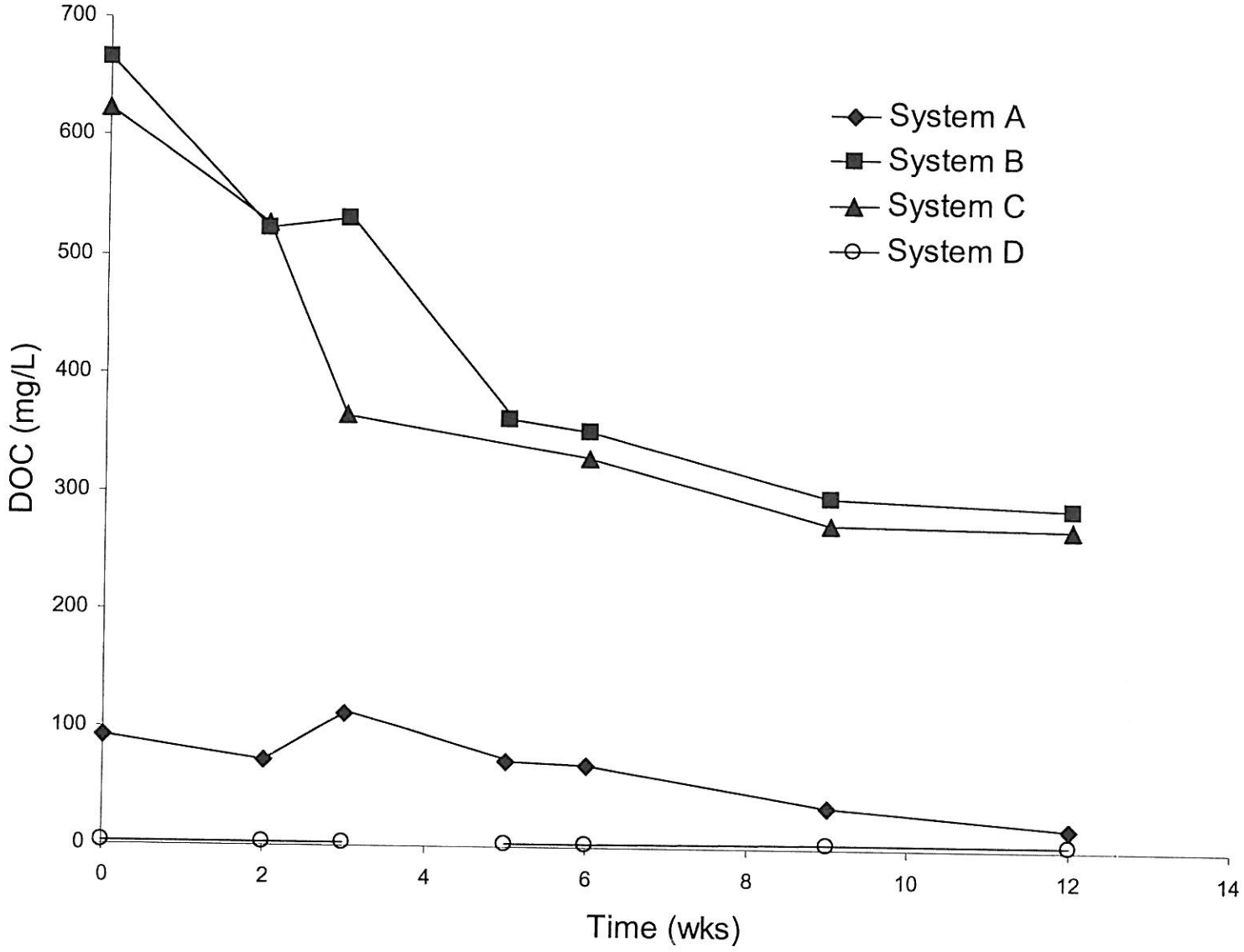

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FIGURE 12
CONCENTRATION OF DISSOLVED ORGANIC CARBON AS A FUNCTION OF TIME MEASURED IN BIOREACTOR BARRELS

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