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IDENTIFICATION OF THE TRANSITION ELEMENTS ASSOCIATED WITH ASBESTOS MINERALS AND THEIR BEHAVIOR IN AQUEOUS SOLUTION

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Magnesium and soluble silicates are liberated from asbestos minerals when the minerals are placed in water. In addition, other elements such as the transition metals, nickel, manganese, cobalt, copper, chromium and vanadium, have been identified in asbestos minerals[1] and may also dissolve from the minerals. The chemical and electrochemical behavior of these metals in the aqueous phase and the possible interactions between them and organic substances may be of great importance in biological systems.

It is well known that the polar side groups of protein molecules (including enzyme structures) in biological systems interact with electrolytes in solution. It is, therefore, reasonable that metal ions liberated from surfaces or edges of asbestos fibers and also localized sites on the fibers themselves may have an effect on the specific activity of such protein molecules.

In the present paper, certain characteristics of the transition trace elements associated with asbestos minerals are discussed. Analyses of such minerals for trace metals are also discussed. In addition, possible reactions between the metallic ions and organic substances are noted.

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Experimental Determination of Trace Metals Present

Chrysotile from Quebec, Canada, and amosite and crocidolite from South Africa were the minerals considered. These minerals were ground in a pebble mill in a manner detailed in a previous paper[2].

Estimation of amounts of selected metals associated with asbestos minerals were made using several different analytical procedures. The techniques

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included colorimetric methods[3,4], proton activation analysis[5] and atomic adsorption[6]. For colorimetric analysis of nickel the oxime method was employed; for cobalt the nitroso-R-salt method in a citrate-phosphate-borate medium was used; for chromium the diphenylcarbazide method after separation of vanadium with 8-hydroxyquinoline was used; for manganese a permanganate method was used. Table I lists the analytical data obtained.

The results obviously vary from one analytical method to another. Also, it is suspected that the ground sample itself has a greater metallic content than the bulk fibers. Accordingly, the metal contents of the ground asbestos samples reported for each type of analytical method will only give a rough idea as to fiber metal content since metal reported may depend on the precise method of sample preparation. However, because of their relative large concentrations, Mn in amosite and Ni in chrysotile must be considered as being more than merely trace elements.

Anyway, the heavy metals identified can dissolve if the aqueous environment of the asbestos fibers is sufficiently acid and/or the environment is such that it contains other substances which react with the metals in such a way as to solubilize them. An example of an aqueous system which apparently solubilizes such metal ions from asbestos minerals is bovine serum[7].

DISCUSSION

Important properties of asbestos minerals - aqueous phase systems include the minerals' surface properties, dissolution of the minerals, the appearance in the aqueous phase of simple and complex metal ions derived from the minerals, and the behavior, including electrochemical behavior, of these ions in the aqueous phase.

The aqueous surface properties have been studied by various researchers

(8,9,10,11,12). Considering the trace metals that potentially can go into solution, these elements may be part of the asbestos mineral's crystal structure, may be present in intimately associated minerals or may be introduced as contaminants during mineral and sample preparation.

The most common minerals associated with chrysotile are magnetite and brucite. Both of these minerals are often found intergrown with the fibers(13). Other trace minerals associated with chrysotile are chromite, calcite, magnesite, olivine, pyroxene, tremolite, actinolite, chlorite, talc and chalcedony. The proportions of these minerals may vary considerably from one deposit to another. Evidently all the chromium is associated with the magnetite phase, most probably as an isomorphous substitution for ferric iron(14). Most of nickel is also found in the magnetic fraction apparently in an iron-nickel alloy, awaruite, whose composition ranges from $FeNi_2$ to $FeNi_3$(15) and in magnetite.

Manganese, cobalt and copper probably come from mineral processing operations. Origin of vanadium detected is not known. Furthermore, because of its interference by iron in analytical techniques used, reported quantities of this metal are in doubt.

For amosite and crocidolite similar sources for metals present probably also obtain except, of course, for manganese which is mainly present in the crystal structure of amosite.

Some properties of these metals will be discussed in view of their thermodynamic and electrochemical behavior.

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Thermodynamic Properties

With the aid of thermodynamic equilibrium data and solubility limits a graphical presentation of the relation between the total metallic ion concentration and hydrogen ion concentration can be constructed.

Figure 1 shows the solubility of the hydroxides of the metals identified

in asbestos minerals as a function of pH (except vanadium). The curves were constructed from data found in Sillén and Martell[16]. At a pH less than 8.5, the equilibrium concentration of each metal is in the order Mg > Mn > Fe(II) > Co > Ni > Cu > Cr. Further, according to the free energy of formation[17] for divalent cations, $G^{\circ}_{Mg^{++}} > \Delta G^{\circ}_{Mn^{++}} > \Delta G^{\circ}_{Fe^{++}} > \Delta G^{\circ}_{Co^{++}} > \Delta G^{\circ}_{Ni^{++}} > \Delta G^{\circ}_{Cu^{++}}$. The significance of the free energy of formation of aqueous ions is that the greater the solubility, the greater the free energy change in solution. Also note that at about neutrality, the approximate pH of the lung, Co(II), Mn(II), Ni(II), Fe(II), and Mg(II) possess considerable solubility.

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Electrochemical Properties

Details of electrochemical equilibrium phenomena may be graphically presented by the potential-pH diagram (or Eh-pH diagram). This diagram is constructed using known standard free energy data of the cations, oxides or hydroxides and their possible reaction products in aqueous solution and calculating from this data the relationship between the two variables, pH and chemical potential. The diagrams consist of "stability" lines which separate stability regions for metal-ligand species studied. Figures 2 and 3 show the Eh-pH diagrams for the Ni, Mn, Cr, Fe, Co, Cu and Mg systems. Also shown are the lower (line a) limit of stability of water and the upper (line b) limit of stability of water. Data for construction of the curves are from Pourbaix[18]. The assumed concentration of the dissolved species of each metal is 10^{-6} mole/liter. In the figures the unshaded areas represent the soluble species and the shaded regions represent either a metallic state or an oxide (or hydroxide) form in the presence of water. Over the shaded regions these solid forms have a total solubility of less than 10^{-6} mole/liter. It should be noted that within the stability limits of water, metallic chromium, iron and manganese will not exist since the oxidation potential for each is well below the lower limit of the

water stability line. However, in the case of nickel, cobalt and copper there is the possibility of the existence of the metallic phase in equilibrium with soluble species. This possibility means that metallic nickel, cobalt and copper can be produced directly from aqueous solution under mildly reducing conditions.

In the asbestos-water system, however, many complications arise because of the sizeable number of elements present. Thus, it is difficult to predict whether a particular metal might or might not be present in metallic form. Also a problem is that in the aqueous solution-asbestos system the potential present is probably a mixed potential. However, Eh of the lung should be of importance in establishing stable forms of the various metal oxides discussed.

Test of the Eh-pH diagram

The thermodynamic equilibrium relations between magnesium ions and pH may be expressed by the equations:

$$Mg^{++} + 2H_2O = Mg(OH)_2 + 2H^+$$

$$\log [Mg^{++}] = 16.93 - 2pH \text{ or } K_{Mg(OH)_2} = 1.82 \times 10^{-11}$$

In an earlier study[2] the present authors measured the dissolution of $[Mg^{++}]$ from chrysotile as a function of time after the mineral had been placed in water (1 gm, -325 + 400 mesh chrysotile, in 100 cc water). After one hour it was found that the solution concentration of $[Mg^{++}]$ was 4.36×10^{-4} M. According to the above equations solution pH should be between pH 10.14 and 10.31. Our actual experimental data varied between pH 9.76 and 10.0. Thus, there is reasonable agreement between theoretical and experimental data. The results further indicate that the surface properties of chrysotile are similar to those of brucite ($Mg(OH)_2$) which is what would be expected if the outer layer of chrysotile consists of magnesium hydroxide. Note, however, that since the next layer consists of silica, which should have a small solubility, it would

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be expected that the pH would be slightly less than calculated based on 100% brucite and this is what was obtained.

The overall dissolution reaction for chrysotile in water may be written as: $Mg_3 Si_2O_5 (OH)_4 + 5 H_2O = 3Mg^{++} + 6OH^- + 2H_4SiO_4$ (soluble)

Using the free energy of formation for each species involved (from Hostetler and Christ[19] and Latimer[17]) in the above reaction, an equilibrium constant for the reaction can be calculated.

From the relation $G^\circ_R = 2.303\ RT \log K$ the equilibrium constant for chrysotile is $K = [Mg^{++}]\ [OH^-]\ [H_4SiO_4]^2 = 10^{-51.8}$

According to our experimental data $[Mg^{++}] = 4.36 \times 10^{-4}$ M, pH = 10.0, and soluble silica $[H_4SiO_4] = 5.33 \times 10^{-5}$. Substituting this data into the above equation, $K = 10^{-48.6}$ which is in reasonable agreement with the published thermodynamic data.

In the case of the trace metals considered, a similar approach comparing calculated and experimental relations may not be made since the total amount of trace metals in solution is too small. However, if those trace elements exist as either dissolved species or at the surface of the mineral fibers, there is always a possibility of their interacting with the surrounding environment even considering their small concentrations. If the surrounding materials have some specific reactivity to these metals this reactivity then should be considered relative to the nature of the probable chemical reaction involved and to kinetics of the reaction.

Recently Cralley[20] suggested with supporting data that the carcinogenicity of asbestos is related to electromative interactions among the heavy metals associated with asbestos minerals. In other works certain organic materials such as n-alkanes, and 3,4 benzpyrene have been identified in asbestos fibers[21].

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Almost all biological reactions fail to proceed at an appreciable rate without enzymes. An important characteristic of enzymes is that side chains can contain ionizable groups, and at physiological pH values contain a number of charged groups. In other words, the polar side chains have the potential to interact with other electrolyts in solution. It is, therefore, apparent that metal ions may often have a pronounced effect on the catalytic activity of enzymes. Thus, the metal ions may directly effect the enzymatic breakdown of organic substances such as 3,4 benzpyrene.

Nickel carbonyl has been shown to induce lung tumors[22]. Note that a heavily exposed asbestos worker who also has smoked heavily over a long time period conceivably has a chance to produce nickel carbonyl in his lung if he has accumulated enough carbon monoxide over this time period and has had small quantities of metallic nickel present in his lungs. An interesting item to speculate about is the Eh in the lung in the immediate vicinity of an asbestos fiber. Is the Eh value such that metallic nickel could be formed? Or, alternately, is the Eh value such that CrO_4^{2-}, another known carcinogen, might become stable and dissolve in significant amounts?

Another item of interest might be the interaction of lung surfactant and ions that can dissolve from asbestos fibers. Lung surfactant apparently consists primarily of dipalmitoyl lecithin[23], an amphoteric substance possessing an isoelectric point near pH7[24]. The unique characteristics of amphoteric surface active substances, necessary for such items as preventing the collapse of aveoli upon expiration, are greatest near their isoelectric point. Changes in pH such as by release of Mg^{2+} and OH^- ions from asbestos minerals may have a profound effect on proper function of lung surfactant. In addition, transition metal ions released by the fibers may have a significant effect on the proper functioning of lung surfactant. These effects coupled with the inhibition

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of enzemes by some transition metal ions plus possible formation of nickel carbonyl may combine to initiate tumors.

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Table I Metals Associated with Asbestos Minerals (ppm)

Element	Colorimetric Analyses		Proton Activation Analyses			Atomic Absorption Analyses	
	Chrysotile	Amosite	Chrysotile	Amosite	Crocidolite	Chrysotile	Amosite
Ni	1240	-	90*, 550**	20*, 530**	340**	774	66.4
Co	50.7	-	2*	-	-	156	31.6
Cr	78.8	-	50*, 20**	50*, 100**	70**	14.4	24.0
Mn	-	6500	360*, 300**	11400*, 11600**	580**	269	-
Cu	-	-	750*, 20**	300*, 10**	100**	14.8	60.4
V	48.8	-	70*	-	-	-	-
Fe	-	-	9.5%*, 8.2%**	30.0%*, 32.0%**	28.0%**	-	-
Ti	-	-	400*, 290**	1050*, 610**	900**	-	-
K	-	-	460**	500*, 880**	1150**	-	-
Ca	-	-	570**	1500*, 1400**	1650**	-	-

* HCl matrix

** HF matrix

Concentration (mole/liter)

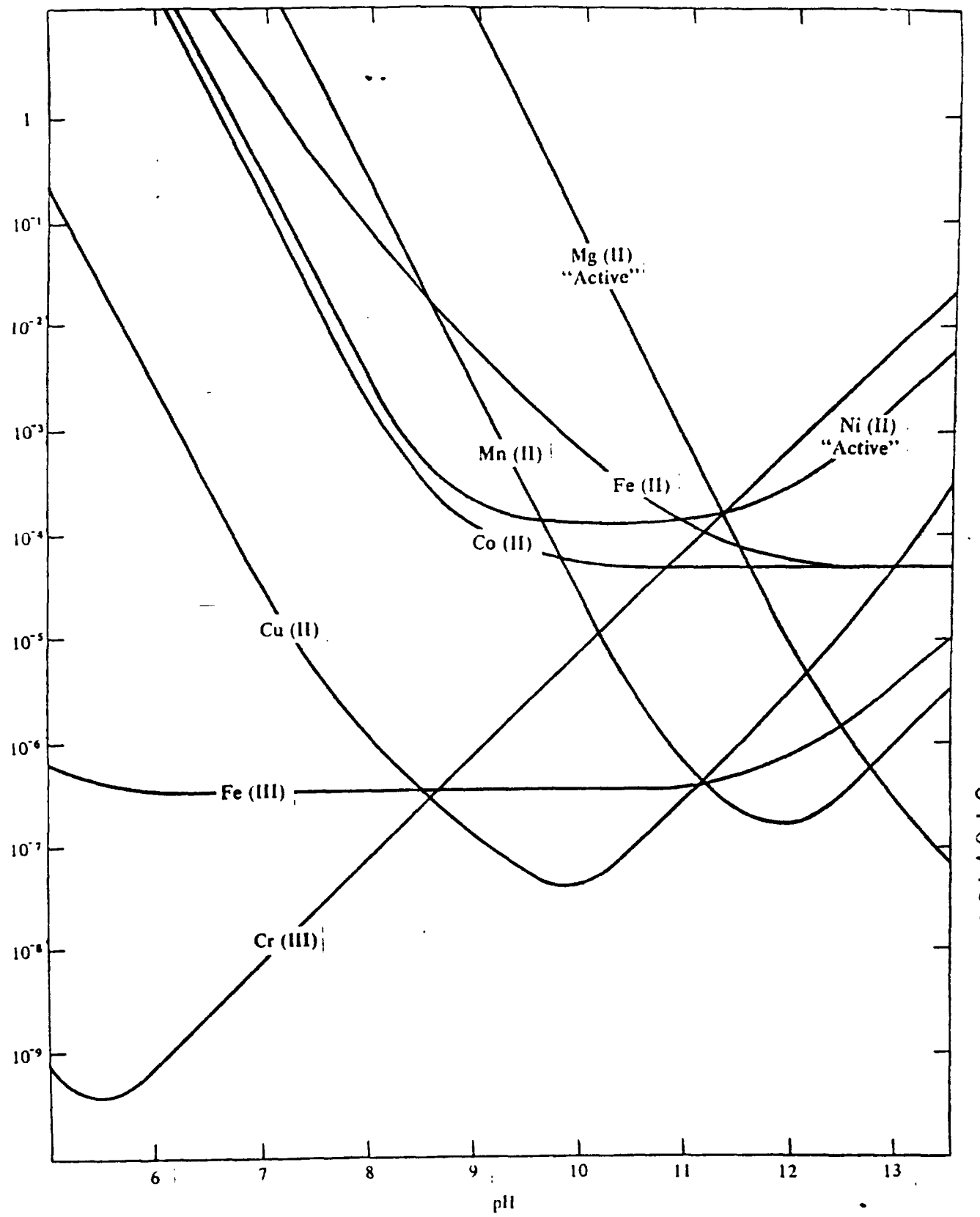

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Fig. 2. Total Solubility of Metal Hydroxides in Water at 20–25 °C.

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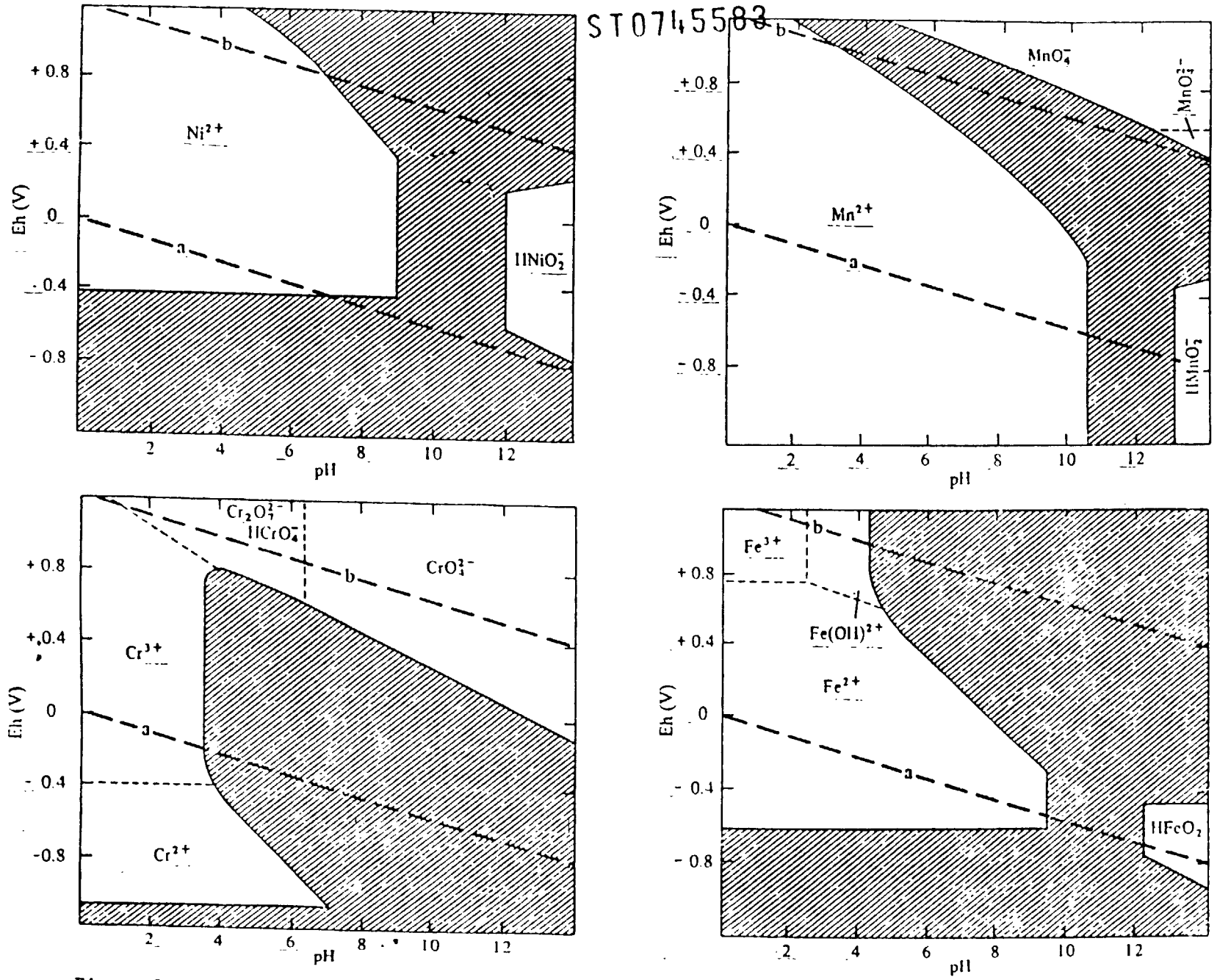

Figure 2. Eh-pH Diagrams for Ni, Mn, Cr, Fe in Aqueous Systems. Shaded Areas are Regions where Non-Soluble Species are Stable Assuming a Total Metal Solubility of 10^{-6} mole/liter

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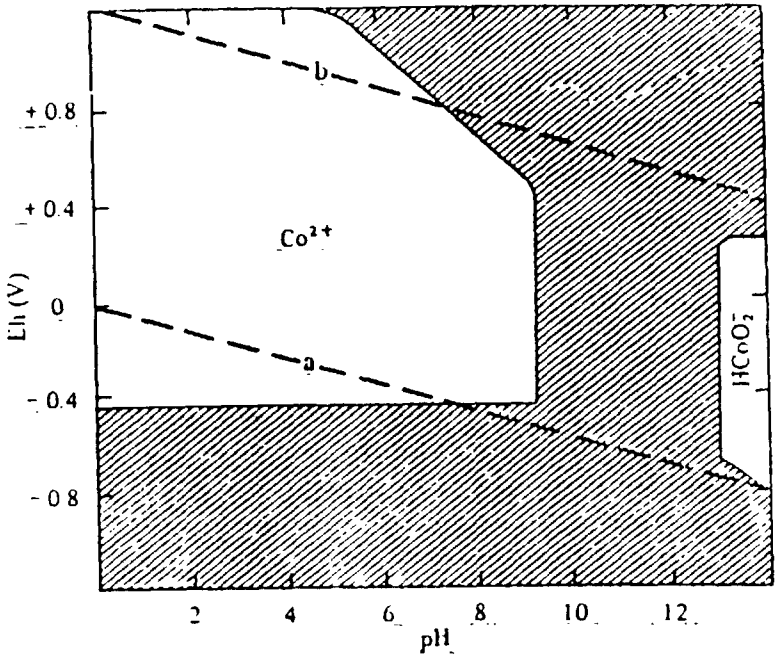

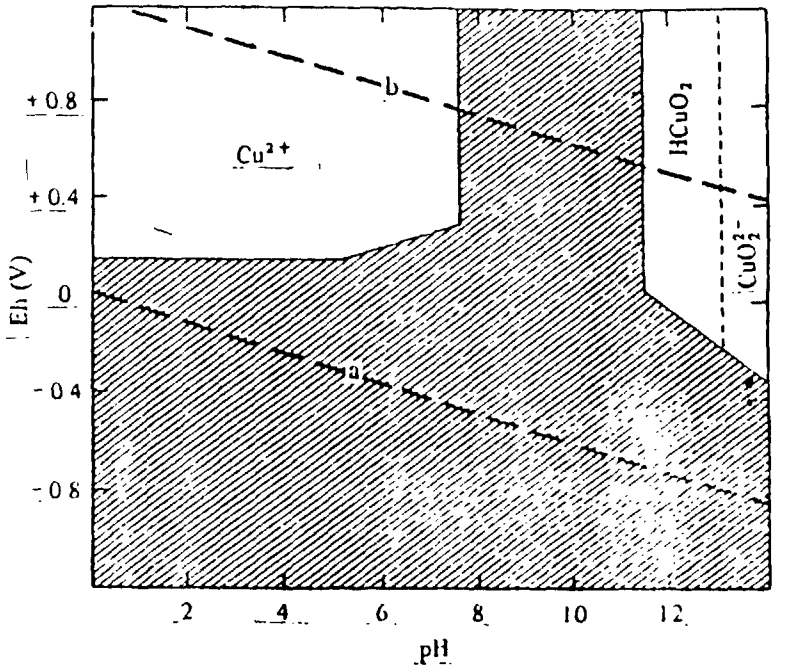

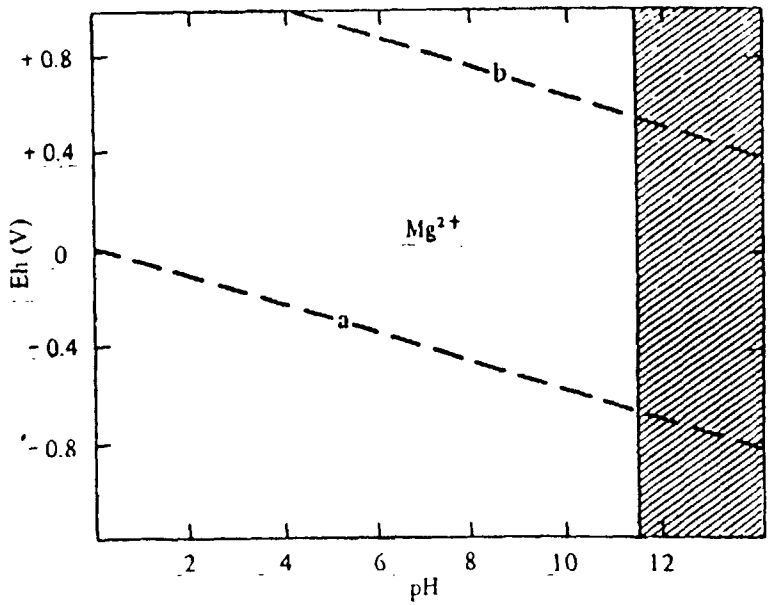

Figure 3. Eh-pH Diagrams for Co, Cu and Mg Aqueous Systems. Shaded Areas are Regions where Non-soluble Species are Stable Assuming a Total Metal Solubility of 10^{-6} mole/liter.

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