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A novel flow process for metal and ore solubilization by aqueous methyl iodide

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Aqueous solutions of methyl iodide (CH_3I) react with metal ores and with metals, causing them to dissolve in water. This dissolution has been investigated in both static extraction and flow systems. Aqueous concentrations of metals are enhanced anywhere from 3- to 242-fold. The proposed mechanism involves electrophilic attack on the solid surface, thereby breaking the linkages binding the metal to the solid lattice and causing dissolution. Because biogenic sources constitute a major component of global CH_3I flux, prospects for related polyfunctional algal haloorganics as aqueous ore or metal solubilizers are noted.

Keywords: Methyl iodide, metal, ores, extraction, methylation

INTRODUCTION

The increasing scarcity of high grade metal ores, environmental concerns and increasing energy costs have made low-energy processing of lean ores an important aspect of metals recovery.[1] Hydrometallurgical processes often employ mineral protic acids,[2] (sometimes in combination with other agents such as phosphate[3] or chloride[4]), and ammonia[5] in aqueous systems for metal dissolution.

Metabolic products of microorganisms such as ferric ions (from oxidation of pyrite) and sulfuric acid are commercially important in copper biohydrometallurgy.[6] Other metabolic products of microorganisms have been shown to solubilize metal ores[7] and bulk metals.[8,9] However, these processes have not been fully characterized or commercially developed.

Recently we showed that methyl iodide (CH_3I), produced globally by marine algae[10] and fungi,[11] reacted with anoxic sediments to release metals into the surrounding water.[12] The anaerobic nature of these sediments suggested that such metals were present as sulfides, and that methyl iodide caused their release by reactions such as the following:[12]

$$FeS(s) + 2CH_3I(aq) \rightarrow Fe^{2+}(aq) + 2I^-(aq) + (CH_3)_2S(g) \qquad [1]$$

Not only pure metal sulfides, but also binary and ternary sulfide ores behaved in this manner. A separate investigation[13] showed that refractory (m.p. = 883°C) SnS reacted with methyl iodide in water to yield a soluble methylated metal product in the following manner:

$$SnS(aq) + 4CH_3I(aq) \xrightarrow{60^\circ} CH_3SnI_3(aq) + (CH_3)_3S^+(aq) + I^-(aq) \qquad [2]$$

Because of our interest in processes involving the methylation of metals and their subsequent transport through water and/or across phase boundaries, we have extended these batch-type experiments with methyl iodide to process stream conditions. We studied the reactions under flow stream conditions to see if they might be of use for metal recovery under industrial or mining conditions. In this paper we describe the reactions of methyl iodide with a wide variety of binary or ternary compounds of metals with nonmetals or metalloids (both as pure compounds and as naturally occurring ores), and also with pure metals, in flow streams to release soluble metal species.

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EXPERIMENTAL

Chemicals

Metal sulfides, selenides, tellurides, arsenides, etc. were obtained from Alfa/Ventron. Methyl iodide was obtained from commercial sources. Ores were purchased as mineralogical specimens and were pulverized into sub-40 mesh particles, being subdivided into various particle sizes upon occasion. Standard reference materials (SRM) samples were obtained from the National Bureau of Standards Reference Materials Office[14] either in the form of pellets or of strips; these latter were cut up as needed.

Flow reactions

The flow apparatus used is shown in Fig. 1. The side-arm glass sample vial was 7.0 cm long and 2.5 cm in diameter. Teflon tubing was attached to the glass inlet and outlet tubes (1 mm i.d.) using plastic glass-to-teflon tubing adaptors (Altex Scientific, Inc.). A weighed quantity of material (usually 5–15 g) was placed on the bottom of the vial. Plugs of glass wool were placed above the ore material. Streams of deionized water or saturated aqueous methyl iodide (approximately 100 mmol dm^{-3})[15] were passed through the substrate as shown in Fig. 1 using a Cole Parmer peristaltic pump and tygon tubing (0.5 mm i.d.). Flow rates ranged from 1.3 to 2.8 cm^3 min^{-1} for varying lengths of time. Aliquots of 0.5–2.0 cm^3 were collected at regular intervals and the levels of dissolved metals were measured after appropriate dilution with deionized water.

Chemical and analytical procedures

Dissolved metal concentrations were measured using a Perkin–Elmer Model 460 Atomic Absorption Spectrometer equipped with a graphite furnace atomizer. Hollow cathode (Fe, Cu, Pb) or electrodeless discharge (As, Sb) lamps were used for specific elements. Standard metal solutions served to prepare calibration curves for each individual experiment.

Chromatographic studies employed a Hewlett–Packard HP-5995 Gas Chromatograph/Mass Spectrometer. Reactions were carried out in closed vessels, into which diethyl ether was injected. The ether was then removed and analyzed.

RESULTS

Chemical compounds

The iron(II) and lead(II) chalconide series (M_aE_b, $a = b = 1$; M = Fe, Pb; E = S, Se, Te) were investigated under flow conditions. Table 1 shows the full results for PbSe and FeTe. With pure water flowing over the solids, there was some initial

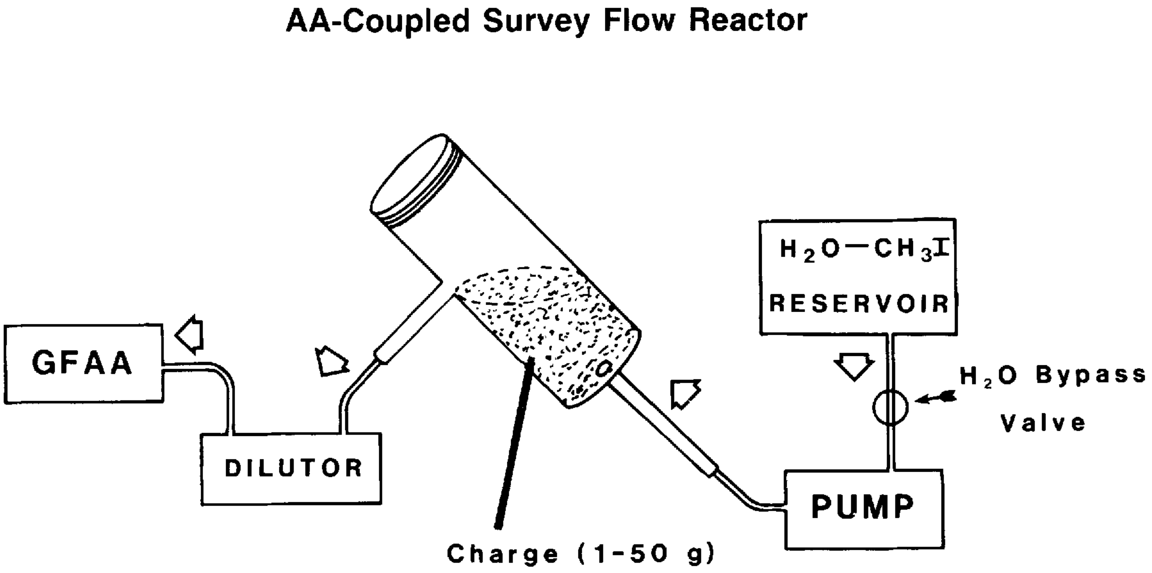

Figure 1 Flow apparatus used in studying metal dissolution by aqueous methyl iodide with detection by graphite furnace atomic absorption spectrophotometry (GFAA).

Table 1 Flow studies on metal dissolution in the presence of aqueous methyl iodide[a]

FeTe		PbSe		Pyrrhotite (FeS)		Stibnite (Sb_2S_3)		SRM 365 (electrolytic iron)	
Time	Fe conc.	Time	Pb conc.	Time	Fe conc.	Time	Sb conc.	Time	Fe conc.
10	0.77	11	6.8	37	2.19	12	5.20	5	ND
20	0.25	35	5.3	52	1.93	26	4.20	10	ND
30	0.08	49	2.3	67	1.44	40	3.70	16	0.01
35	0.11	62	3.4	83	0.97	80	4.82	21	0.05
-36-	CH_3I started	88	4.3	99	0.79	139	1.88	26	0.01
		100	6.7	113	0.71				
40	1.85	112	4.1	129	0.61	-143-	CH_3I started	-27-	CH_3I started
45	2.88	139	2.7	148	0.18	150	2.99	30	0.47
50	1.81	157	6.6	180	0.11	166	2.94	35	3.08
65	1.78	-159-	CH_3I started	-182-	CH_3I started	187	4.87	40	3.94
70	1.67					216	7.38	46	4.66
-71-	H_2O resumed	175	15.0	196	0.19	226	8.59	51	4.89
		195	51.6	215	0.26	244	7.90	57	5.93
75	0.10	211	70.2	234	0.50	270	18.3	60	6.33
80	0.04	229	64.8	252	1.19			63	6.53
85	0.04	265	60.6	285	1.92			-64-	H_2O resumed
90	0.14	284	56.4	302	5.90				
		304	75.4	335	6.00			65	3.70
		-319-	H_2O resumed	354	5.70			67	2.74
				398	7.06			70	0.61
		332	14.3	429	8.03			75	0.26
		345	17.6					80	0.19
		357	14.8					90	0.19
		382	15.8					96	0.17
								106	0.17

[a] All times are in minutes. All concentrations are in parts per million (mg metal dm^{-3} water) except SRM 365, which is in parts per billion. The flow rates were approximately 2.0 $cm^3 min^{-1}$, except for the SRM 365 experiment which was 2.4 $cm^3 min^{-1}$.

dissolution, perhaps enhanced by the presence of minute solid particles physically swept up in the current. When the flow of aqueous methyl iodide began, the concentration of dissolved metal increased sharply. Levels remained high, though variable, as long as the methyl iodide flow continued. When the deionized water flow was resumed, the concentrations of soluble metal decreased markedly. Table 2 lists the extent of solubility magnification for various compounds.

Ores

A variety of ores, mostly sulfides, such as pyrrhotite (FeS) and stibnite (Sb_2S_3), were obtained and pulverized into powders of varying particle size. These were treated in the same manner as the chemical compounds. Enhancement of metal dissolution improved when the ore samples were washed before starting the flow of water. As Tables 1 and 2 indicate, the ores behaved in the same way as pure chemical compounds.

Pure and alloyed metals

Various forms of iron and copper and their alloys were also studied using the flow method. Electrolytic iron (SRM 365) showed very great enhancement of dissolution with methyl iodide, while steels (SRM 8j & 15g)[14] showed lesser enhancement. When repeated alternating cycles of water and aqueous methyl iodide were employed, the enhancement of concentration steadily increased, as shown in Fig. 2. Small iron nails used as substrate gave similar results.

Treatment of commercial electronic circuit boards showed that aqueous methyl iodide solutions removed copper films (0.025 mm) after 5 d at 60°C. For comparison, an equimolar solution of HNO_3 did not show as extensive dissolution

Table 2 Concentration enhancement by methyl iodide in flow runs

	Soluble metal concentrations ($\mu g\ g^{-1}$)		
	Initial	Maximum	Magnification
Pure compounds			
FeS[a]	0.503	22.3	44.3
FeSe[a]	0.0874	12.6	144
FeTe[a]	0.080	2.88	36
PbSe[b]	6.6	75.4	11.4
PbTe[b]	0.060	8.72	145
Ores			
Pyrrhotite (FeS)	0.108	8.30	76.9
Chalcopyrite ($FeCuS_2$)[a]	0.0107	0.256	23.9
Galena (PbS)	5.10	133	26.1
Stibnite (Sb_2S_3)	1.38	18.3	13.3
Nicolite (NiAs)[c]	0.92	59.7	64.9
Metals			
SRM 365 (Fe)[d]	0.0154	0.200	13.0
	0.0091	0.230	25.2
	0.0013	0.0852	65.5
SRM 8j (Fe)[e]	0.372	1.88	5.05
	0.219	1.41	6.44
SRM 15g (Fe)[f]	0.302	0.783	2.59
	0.634	2.23	3.52
Wire brads (Fe)	0.098	0.645	6.58

[a]Concentration of Fe measured. [b]Concentration of Pb measured. [c]Concentration of As measured. [d]99.90% Fe; 0.073% other metals; 0.26% nonmetals. [e]98.951% Fe; 0.738% other metals; 0.311% nonmetals (Bessemer steel). [f]99.213% Fe; 0.567% other metals; 0.220% nonmetals (open-hearth steel).

of copper as with methyl iodide. Microscopic examination of the copper film surface that had been treated with methyl iodide clearly revealed the leaching effect of that solution. Treatment of stainless steel chips showed marked enhancement of iron dissolution (10–100×) over controls. Dissolution of iron was enhanced at higher temperatures. Treatment of the aqueous reaction system with ultraviolet radiation enhanced the dissolution of Fe. However, irradiation in the presence of methyl iodide did not result in further enhancement of Fe dissolution.

DISCUSSION

In one sense the reaction of methyl iodide with elements of Groups V and VI, and with metals, has been known for many decades, albeit under anhydrous conditions. In 1849, Edward Frankland reacted zinc with methyl iodide to form dimethylzinc,[16] and the direct reaction between methyl iodide and the chemical elements occurs for much of the Periodic Table.[17] Similarly, the oxidative addition of other alkyl halides to elements such as sulfur, selenium, phosphorus and arsenic has been extensively reported in the chemical literature. Reaction of aqueous methyl iodide with iron selenide or iron telluride gave malodorous solutions. Extraction of these with diethyl ether and subsequent analysis by gas chromatography/mass spectrometry indicated the presence of both $(CH_3)_2Se$ and $(CH_3)_2Se_2$ in the first case, and $(CH_3)_2Te$ only in the second.

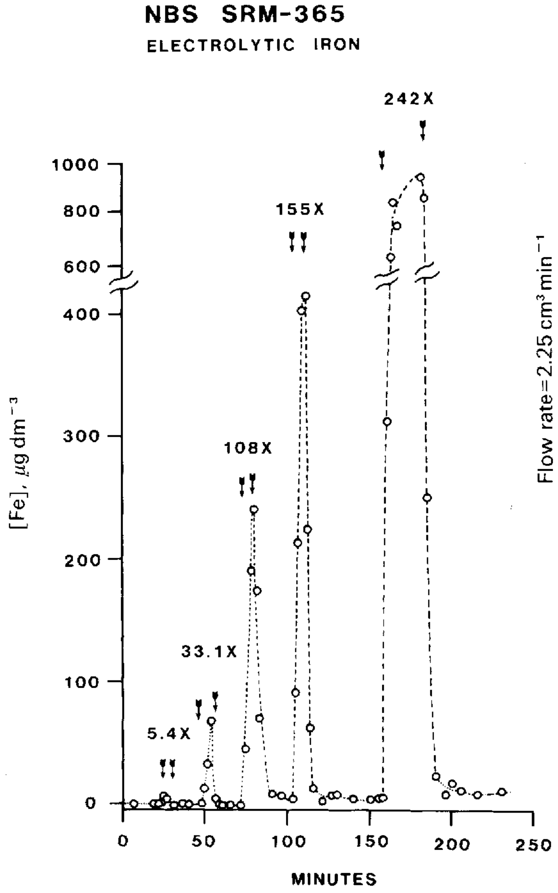

Figure 2 Enhancement of iron dissolution by alternating cycles of aqueous methyl iodide and deionized water (shown by paired arrows where the first arrow denotes the start of methyl iodide treatment).

Reaction of ethyl iodide with iron selenide analogously gave both $(C_2H_5)_2Se$ and $(C_2H_5)_2Se_2$.

The uniqueness of the process described in this paper is in the use of this reaction to cause refractory materials to dissolve in water under simulated process flow streams. We previously proposed a heterolytic mechanism to explain this dissolution phenomenon for solid metal sulfides.[12] This meachnism can readily be extended to incorporate metal selenides, tellurides, phosphides, arsenides, antimonides, and probably other binary compounds (borides, nitrides, silicides, carbides) where the nonmetal (E) is electron-rich relative to the metal (M) in a typical refractory covalent —M—E—M—E— mineral polymer.

$$M_aE_b(s) + abCH_3I(aq) \rightarrow aMI_b(aq) + b(CH_3)_aE(g) \qquad [3]$$

This mechanism would apply to either the pure compound or the naturally-occurring ore; both follow the same pattern of reaction. Bonding of a methyl group to the nonmetal atom causes cleavages of a bond between the nonmetal and the metal in the M_aE_b lattice. Continuing such cleavages eventually causes the metal to be detached altogether from the lattice and move into the supernatant water. Thus the solubility of metal chalconides becomes enhanced in the presence of methyl iodide. The actual degree of solubility enhancement depends on the specific system, but as a general rule, the less soluble the compound is, the greater the relative enhancement in the presence of methyl iodide. Reaction rates would be enhanced at higher temperatures. We showed that dissolution of SnS[13] and Cu^0 by methyl iodide increased when the temperature was raised from 22°C to 60°C. Certain metals in lower oxidation states (Sn(II)), As(III)), which can appear in binary or ternary forms, may themselves undergo oxidative methylation by methyl iodide to form methylmetals,[13] analogous to formation of $(CH_3)_4Sn$[18] and $(CH_3)_4Pb$[19] from the free metals.

The reaction for methyl iodide with metals, as previously metioned, is well established and is widely used for synthesis of methylmetals, most commonly in the Grignard reaction. All such preparations, however, are done under strictly anhydrous conditions, with the intention of either isolating the methylmetal or preserving it for use as a reagent for synthetic purposes. In the presence of water many metal–carbon bonds are rapidly cleaved, especially if the metal is active, as most transition metals are. Certain derivatives, such as methylpentaaquochromium(III) ion, are stable enough to be used as methylating reagents in water.[20] However, such a metal–carbon bond must form *before* it can be cleaved, and the process of formation removes the metal from its lattice. A possible mechanism might be written as follows:

$$M(s) + CH_3I(aq) \rightarrow M.CH_3I(s) \qquad [4]$$

$$M.CH_3I(s) \rightarrow CH_3MI(aq) \qquad [5]$$

$$CH_3MI(aq) + H_2O(1) \rightarrow CH_4(g) + MI^+(aq) + OH^-(aq) \qquad [6]$$

The electrophilic carbon atom of methyl iodide attaches to the electron-rich metal surface. There it undergoes oxidative addition to a metal atom, forming a CH_3MI molecule. The metal, as a result, becomes removed from its lattice. The CH_3MI then moves into the water layer, where the active metal–carbon bond undergoes hydrolysis, resulting in a hydrated cationic metal species that remains dissolved.

Methylation in both compounds and pure metals involves an initial attachment of methyl iodide at the surface of the solid. In the case of pure metals, this continuing process would cause the uncovering of fresh new reactive surfaces, thereby accelerating the rate of reaction. Experiments involving repeated methyl iodide–water alternating cycles showed an enhancement of dissolution with each successive cycle, as illustrated for metallic iron in Fig. 2. The relative degree that CH_3I versus water contributes to the dissolution of the substrates is uncertain at this time, though water itself causes disintegration of mineral fibers on long standing by leaching or hydration processes.[21]

It is our belief that this process has many possible uses in mining and metallurgy, including (but not limited to): recovery of metals (especially the heavier and rarer metals) from chalconide ores; recovery of metals at low levels from inaccessible sources such as scrap and wastes; and selective dissolution of alloys or mixed ores. A practical example of this last case might be metal films or coatings on used circuit boards, which could be treated with methyl iodide and the metals thereby recovered.

Our observations suggest that best results might be obtained in a cycling system, employing alternating flows of water and aqueous methyl iodide. It is worth noting that the (covalent) iodide is converted to either I^- or I_3^-, either of which might be used to form I_2 and reacted with methane to form more methyl iodide. Other alkyl iodides reacted with metals in similar fashion, and might be used in place of methyl iodide under some circumstances. We are currently investigating these possibilities.

Algae or fungi would likely be the most inexpensive means of generating methyl iodide, perhaps in outdoor lagoons or treatment ponds. We showed[22] that methyl iodide could be generated from reaction of I^- with dimethylpropiothetin ($(CH_3)_2S^+CH_2CH_2COO^-$, DMPT), an important metabolite in the sulfur metabolism of many algae. The addition of I^- to DMPT, to whole cells of microorganisms or to lysed cells are potential process engineering considerations for methyl iodide biogenesis. The use of thermophilic strains of organisms could enhance reaction rates. However, the biochemistry of methyl iodide production is not completely understood and should be investigated. This is especially important in view of the growing literature demonstrating the global availability, in amounts greater than methyl iodide, of other biogenic halogenated organic molecules such as bromoform, chloroform, dibromomethane, halogenated acetones, chlorinated and brominated phenols, and others.[23,24] These molecules possess properties sufficiently similar to methyl iodide to suggest they may also enhance metal solubility. For example, such compounds also possessing keto and imido groups, may further enhance metal solubilization through chelation to the metal atom. Furthermore, more than 40 diverse haloorganic metabolites alone were identified in the edible Hawaiian red seaweed, *Asparagopsis taxiformis*, incorporating ketonic, allylic, hydroxy, or polyhalo (Br, Cl, I) functions.[24] In view of reports that methyl iodide hydrolyses slowly in seawater to CH_3OH,[25] and this also exhibits Cl-dependent solubilization of bulk nickel,[26] and π-allylic ligands can strongly ligate many metals,[27] we envisage a substantial vista for research and development of the 'aquatic direct reaction' in dissolution of metals by biogenic haloorganics as outlined by this inaugural paper.

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Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose. Studies conducted at NBS were partially sponsored by the US Office of Naval Research.

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