THE SYNTHESIS OF MERCURY JAROSITE AND THE MERCURY CONCENTRATION IN JAROSITE-FAMILY MINERALS

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ABSTRACT

The factors affecting the composition and yield of mercury jarosite $Hg_{0.5}Fe_3(SO_4)_2(OH)_6$ during synthesis by the preferred slow-addition technique have been studied. The yield is strongly dependent on the pH of the hot ferric sulfate solution, and no jarosite is formed at pH $<$ 1.4; the mercury concentration of the jarosite declines slightly with increasing pH. For a given rate of mercury addition, the product yield increased directly with increasing temperature or ferric ion concentration, but the mercury content of the product is nearly independent of either variable. Once an excess of mercury was pumped, both the yield and mercury concentration of the jarosite were essentially independent of the amount of mercury added, the pumping time and the pumping rate. The partition coefficients for mercury distribution between the solution and jarosite phase have been determined in both the Hg–K and Hg–Na systems. Dilute solutions of mercury in the Hg–Na system are nearly ideal, but potassium is preferentially precipitated in the Hg–K system. Several jarosite-family minerals were analyzed for mercury: none contains more than 0.08 wt. % Hg.

Keywords: jarosite, mercury jarosite, synthesis.

SOMMAIRE

On a étudié les facteurs qui influencent la composition et la production de jarosite mercurifère $Hg_{0.5}Fe_3(SO_4)_2(OH)_6$ pendant la synthèse par la technique préférée d'addition lente. Le rendement dépend fort du pH de la solution chaude de sulfate ferrique; la jarosite ne cristallise pas si le pH est inférieur à 1.4. La teneur en Hg de la jarosite diminue légèrement quand le pH augmente. Pour un taux donné d'addition du mercure, le rendement augmente directement avec la température et la concentration en Fe^{3+}, mais la teneur en mercure du produit est presque indépendante de ces deux variables. En présence d'un excès de mercure, la quantité du produit et sa teneur en Hg ne dépendent ni de la quantité de Hg ajoutée, ni de la durée de la synthèse, ni du taux de pompage. On a déterminé les coefficients de partage du mercure entre solution et jarosite pour les systèmes Hg–K et Hg–Na. Les solutions diluées de Hg dans le système Hg–Na sont quasiment idéales, mais le potassium précipite préférentiellement dans le système Hg–K. On a déterminé la teneur en Hg de plusieurs minéraux de la famille des jarosites; aucun échantillon n'en contient plus de 0.08% en poids.

(Traduit par la Rédaction)

Mots-clés: jarosite, jarosite mercurifère, synthèse.

INTRODUCTION

The jarosite family of compounds, $MFe_3(SO_4)_2(OH)_6$, where M is H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, Tl^+, $\frac{1}{2}Pb^{2+}$ or $\frac{1}{2}Hg^{2+}$, is of interest to mineralogists and metallurgists alike. Jarosite-type compounds are found wherever sulfides undergo strong oxidation under acidic (pH $<$ 3) conditions; they are especially prevalent in the oxidized portions of sulfide ore deposits (Kubisz & Zabinski 1958, Palache *et al.* 1951), where they can constitute a minor source of lead or silver. From a metallurgical point of view, the hot precipitation of jarosite-type compounds has found extensive application in the zinc industry as a means of controlling dissolved iron, and their use in other hydrometallurgical systems is being contemplated (Dutrizac 1979).

Mercury jarosite is one of the least studied of all the jarosite-type compounds, and only a few publications discuss its formation, properties or possible occurrence in nature. Dutrizac & Kaiman (1976) prepared a mercury jarosite using a slow-addition technique that consisted of pumping a slightly acidified solution of $Hg(NO_3)_2 \cdot H_2O$ into a hot ferric sulfate medium. They reported X-ray powder-diffraction data for their material, which contains 14.6% Hg, 35.7% Fe and 28.4% SO_4 (theory: 17.9% Hg, 34.2% Fe and 29.8% SO_4). In that investigation, no attempt was made to study in detail the factors affecting the synthesis of mercury jarosite, and no other studies on the formation of mercury jarosite exist in the literature.

Although a mercury jarosite might be expected to form in the oxidized portions of

mercury sulfide deposits, such a mineral has not yet been identifed (Fleischer 1980). Furthermore, study of the minerals of oxidized mercury deposits has failed to locate even a mercury-bearing jarosite containing significant ($>$ 0.5%) mercury (Razenkova & Samoilova 1972, Zubov & Garbuz 1967, Novikova 1957).

The first objective of the present investigation was to elucidate the factors affecting mercury jarosite formation by the slow-addition technique and to ascertain whether other techniques of synthesis are applicable to this compound. The second general objective was to examine jarosite-family minerals from a number of locations, especially from mercury deposits, to see whether any contain significant concentrations of mercury. This study also deals with the use of synthesis data to explain the general lack of mercury in naturally occurring jarosite-type compounds.

EXPERIMENTAL

Reagent-grade chemicals were used for all experiments. The various techniques applicable to the synthesis of jarosite-type compounds have been described (Dutrizac & Kaiman 1976). Basically, the preferred slow-addition technique consists of slowly pumping a solution of a mercury salt [$Hg(NO_3)_2 \cdot H_2O$] into one litre of hot ferric sulfate medium contained in a two-litre reaction kettle. Four millilitres of HNO_3 were added to the mercuric nitrate solution to dissolve oxy-compounds of mercury. Variables include the composition, pH and temperature of the ferric sulfate solution, as well as the composition of the mercuric nitrate solution and associated physical factors such as pumping rates and the degree of seeding. The mercury jarosite product was subjected to washing in cold, dilute acid and in distilled water; the final product was dried for 24 hours at 110°C. The synthetic products were analyzed chemically, and all the precipitates were examined by a Guinier–de Wolff precision focusing camera to ascertain whether impurity phases were present and to confirm that a jarosite-type compound had been formed. Since the patterns were essentially identical to those indexed in a

previous study (Dutrizac & Kaiman 1976), the compounds prepared in the present program were not precisely measured and indexed.

The jarosite-family minerals were examined using a combination of three techniques. The samples were X-rayed using a Debye–Scherrer camera to confirm the presence of jarosite-type minerals. Where relatively pure, massive material was available, a bulk sample was subjected to wet-chemical analysis. All samples were mounted in polished sections and were probed with a MAC 400 electron microprobe; the data were corrected using a modified version of the EMPADR VII computer program of Rucklidge & Gasparrini (1969). Mercury was determined using the Hg $M\alpha$ line and a 100 s counting period; a 1–2-μm diameter beam was used. Either synthetic Pd_3HgTe_3 or natural cinnabar was used as a Hg standard, and the 3σ detection limit for Hg was calculated by the method of Goldstein & Yakowitz (1975). Some of the samples were also examined on a scanning electron microscope (SEM) with energy-dispersion analyzer and backscattered electron imagery.

RESULTS AND DISCUSSION

Preliminary investigations

Preliminary test work confirmed the importance of good agitation to prevent the mercury jarosite from tenaciously coating the vessel walls (Dutrizac et al. 1980); consequently, all work was done in a well-stirred 2-litre reaction kettle fitted with titanium baffles to ensure good mixing. The effect of the addition of mercury jarosite seed was also determined. Various amounts of seed were added to a solution containing 0.3 M Fe^{3+} (as SO_4) and 0.01 M H_2SO_4 at 98 $\pm$ 2°C; 120 ml of solution containing 8 g $Hg(NO_3)_2 \cdot H_2O$ were pumped at 6 ml per hour into the hot ferric sulfate solution. The effect of the seeding on the yield and on the mercury content of the product is shown in Table 1; the mercury concentrations are comparatively low because less than stoichiometric quantities of mercury were pumped. Although the presence of seed has little effect on the mercury concentration of the precipitate, seeding slightly increases the yield of the jarosite-type product; moreover, previous work has shown that seeding prevents the formation of other basic iron sulfates under marginal synthesis conditions. For these reasons, all subsequent work was done using either one or two grams of mercury jarosite seed.

Guinier X-ray-diffraction analysis of prod-

TABLE 1. EFFECT OF SEED ON MERCURY JAROSITE FORMATION

Seed (g)	Product yield (g)	Wt % Hg	X-ray
0	23.1	7.95	mercury jarosite
0.5	25.8	8.74	mercury jarosite
1.0	25.0	7.06	mercury jarosite
1.5	30.3	7.74	mercury jarosite
2.0	30.0	8.01	mercury jarosite

ucts prepared under a variety of conditions indicated major mercury jarosite together with trace-to-minor amounts of one or more poorly crystallized unknown compounds having broad lines at d values of 10.8, 6.2, 4.55, 3.75, 3.48, 3.16 and 2.74 Å. Since the same unknown material had been detected during the preparation of lead jarosite, it would appear to be a basic iron sulfate containing no mercury. Some of the precipitates also contain small amounts of $HgSO_4 \cdot 2HgO$. Various washing procedures were tried to eliminate the impurities without affecting the mercury jarosite. The procedure finally adopted consisted of three one-litre washes with 0.3 M H_2SO_4 at 25°C, followed by filtration and hot-water washing. Use of hot H_2SO_4 or more concentrated acid media caused the leaching of the mercury jarosite itself. This washing procedure effectively eliminated the $HgSO_4 \cdot 2HgO$ impurity, but did little to alter the amount of the unknown iron compound (which, incidentally, makes the mercury jarosite a dark yellow color as opposed to the bright yellow of the alkali jarosites). Hence, all the synthetic products reported contained a trace amount of this unknown iron compound.

Conditions in the reaction vessel

Figure 1 shows the effect of initial pH on both the yield and mercury concentration in the synthetic jarosite. The pH of the 0.3 M Fe^{3+} solution was adjusted with either H_2SO_4
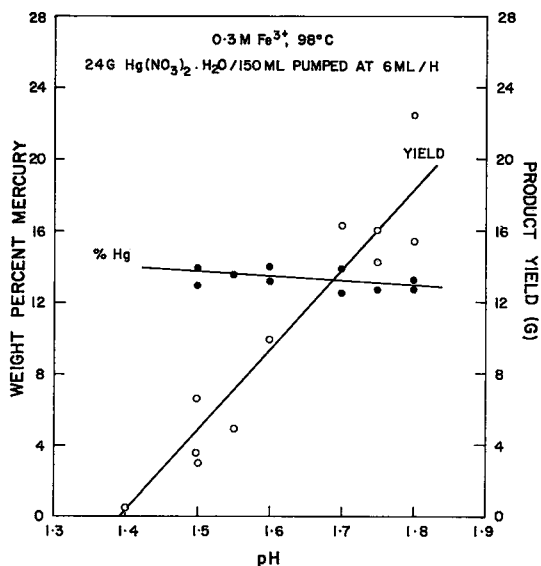

FIG. 1. The effect of the initial pH of the 0.3 M Fe^{3+} solution on the yield and mercury concentration of the synthetic jarosite.

or Li_2CO_3, since lithium does not form a jarosite-type compound. The hydrolysis reaction itself produces acid, which lowers the pH during the course of the reaction:
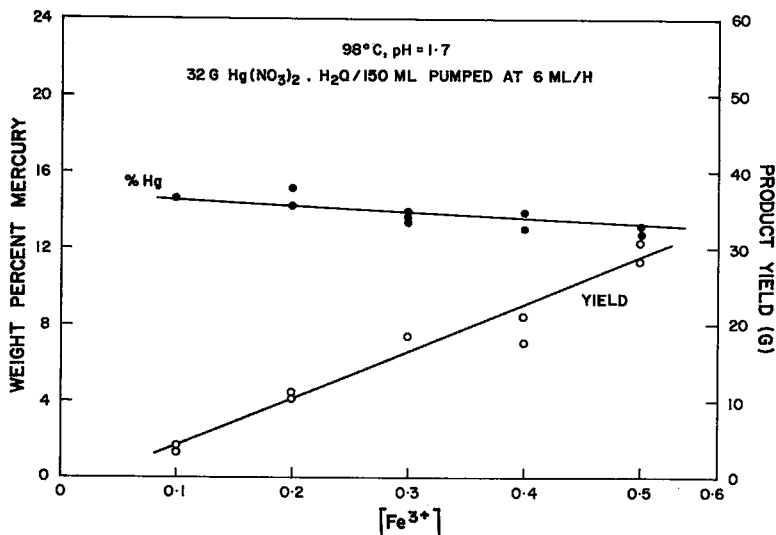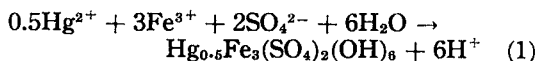
$$0.5Hg^{2+} + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow$$
$$Hg_{0.5}Fe_3(SO_4)_2(OH)_6 + 6H^+ \quad (1)$$

FIG. 2. The effect of the initial Fe^{3+} concentration on the yield and mercury concentration of the product. The Hg^{2+}/Fe^{3+} ratio was different for each experiment.

Also, the mercuric nitrate solution contains 4 ml HNO₃, which is gradually pumped, and this further lowers the pH in the reaction vessel. In these systems, nitrate is a neutral counter ion that does not enter the jarosite lattice and does not seem to affect the reaction. These experiments were all done at 98 ± 2°C and in the presence of 1 g mercury jarosite seed; 24 g $Hg(NO_3)_2 \cdot H_2O$ in 150 ml of solution were pumped at 6 ml *per* hour into the hot solution.

The pH of the iron sulfate solution exercises a major influence on the amount of product formed. Reaction 1 is reversible, and increasing the proton concentration pushes the reaction in favor of the dissolved species. No product was found at pH values of less than 1.4; this suggests that no jarosite was formed and that the 1 g of seed also dissolved during the 24-hour reaction period. Increasing the pH increases the yield of product but slightly lowers its mercury concentration; also, above pH = 1.8 the product becomes difficult to filter; this fact, together with the lower Hg content, indicates the formation of amorphous iron compounds. Of all the jarosites studied, the mercury member seems to be the most sensitive to acid concentration, and even minor variations in pH can give rise to substantial differences in the amount of product. Because the current effort was concerned with the production of significant quantities of material with high mercury levels, an initial pH of 1.7 was selected as the "best" value for subsequent work.

Figure 2 illustrates the effect of the initial Fe^{3+} concentration on both the yield and composition of the mercury jarosite product. The yield of mercury jarosite increased with increasing Fe^{3+} concentration, indicating that the reaction is under iron control and that there is adequate Hg^{2+} available at all iron concentrations. The mercury concentration of the product drops slightly with increasing initial iron concentration, but the effect is not very pronounced. The ratio of Hg^{2+}/Fe^{3+} decreases as the Fe^{3+} concentration increases, and such a change in this ratio is known to decrease slightly the iron concentration of the mercury jarosite (Fig. 5). Attempts to prepare a jarosite-type compound at low iron concentrations (< 0.1 M Fe^{3+}) resulted in the formation of an amorphous reddish iron phase and $HgSO_4 \cdot 2HgO$.

The results presented in Figure 2 were obtained by pumping a fixed weight of Hg^{2+} into a solution containing different iron concentrations, *i.e.*, the Hg^{2+}/Fe^{3+} ratio was different in each experiment. Figure 3 shows the effect of the iron concentration, at a constant ratio of Hg^{2+}/Fe^{3+}, on the yield and concentration of the mercury jarosite product. The amount of $Hg(NO_3)_2 \cdot H_2O$ in the pumping solution was varied so that there were 11 g $Hg(NO_3)_2 \cdot H_2O$ for every 0.1 M Fe^{3+}. All the solutions pumped contained 4 ml HNO₃ regardless of the amount of mercury present. Again, the yield of product increases steadily as the iron concentration increases, indicating product control by iron and
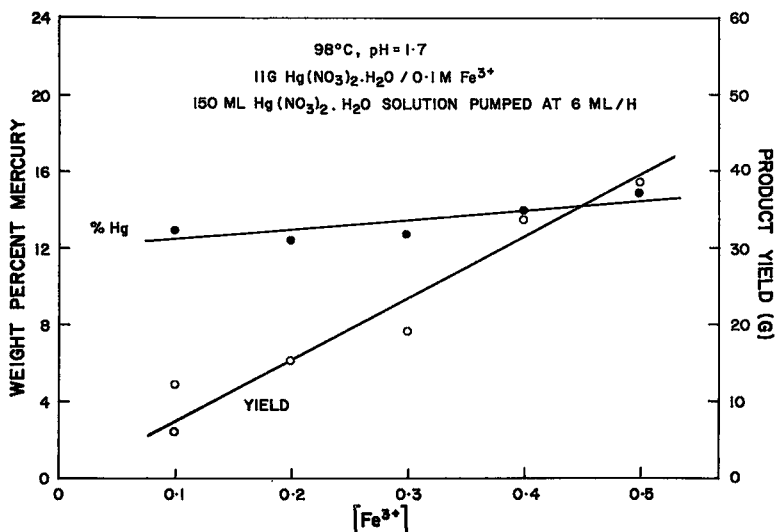

FIG. 3. The influence of the initial Fe^{3+} concentration on the yield and mercury concentration of the product where the Hg^{2+}/Fe^{3+} ratio was constant.

not by mercury availability. The mercury was always present in stoichiometric excess. The mercury concentration in the product increases slightly as the iron concentration increases. A comparison of Figures 2 and 3 suggests that an iron concentration of about 0.3 M is a satisfactory compromise for producing a good yield of product with a high percentage of mercury. One of the surprising features of mercury jarosite synthesis is that the product composition is nearly independent of the Hg^{2+}/Fe^{3+} ratio once a stoichiometric excess of Hg^{2+} is available. Similar results have, however, been noted during the synthesis of alkali jarosites and for the formation of lead jarosite from "solid" $PbSO_4$ (Dutrizac *et al.* 1980).

The effect of the temperature of the 0.3 M Fe^{3+} (as sulfate) solution on both the yield and composition of the mercury jarosite product is shown in Figure 4. The temperature has only a very slight influence on the composition of the product; there is a suggestion that the mercury concentration increases with temperature, but the effect, if any, is masked by the normal scatter of the data. The product yield increases systematically with temperature, and this clearly indicates the desirability of conducting the synthesis at as high a temperature as possible.

Pumping conditions

The experiments described above define the preferred conditions for operating the hot ferric sulfate reaction vessel during the synthesis experiments. The other major part of the slow-addition method relates to the composition of the mercuric nitrate solution and the rate at which it is delivered to the hot iron medium. The Hg^{2+} ion hydrolyzes readily, and an acidic medium must be provided to retard hydrolysis. It was found that the addition of 4 ml concentrated HNO_3 to the mercuric nitrate medium produces a clear solution for all concentrations studied; this practice was followed throughout.

The effect of the quantity of $Hg(NO_3)_2 \cdot H_2O$ in the 150 ml of solution pumped at 6 ml *per* hour into the hot ferric sulfate medium on the mercury concentration of the mercury jarosite product is shown in Figure 5. The theoretical amount of $Hg(NO_3)_2 \cdot H_2O$ needed to react with all the 0.3 M Fe^{3+} solution is 17.6 g. In fact, the actual requirement is less, (1) because less than half the iron actually precipitates and (2) because the mercury jarosite is not stoichiometric. It has been shown (Dutrizac & Kaiman 1976) that all jarosite-type compounds contain a significant substitution of hydronium ion (H_3O^+) in the cation position, *i.e.*, mercury
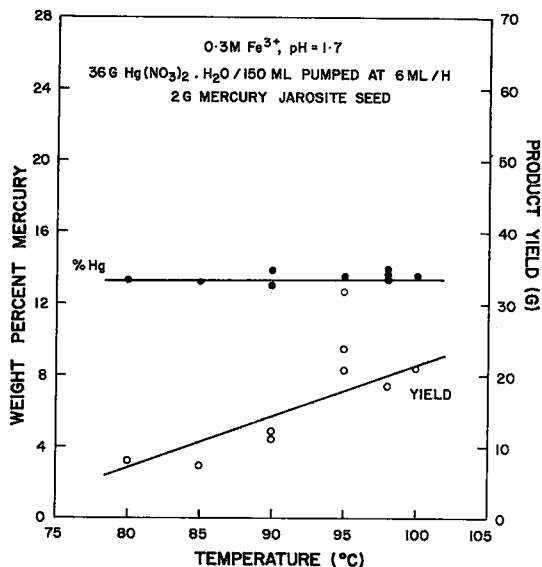

FIG. 4. Variation of the product yield and mercury concentration of the jarosite as a function of synthesis temperature.
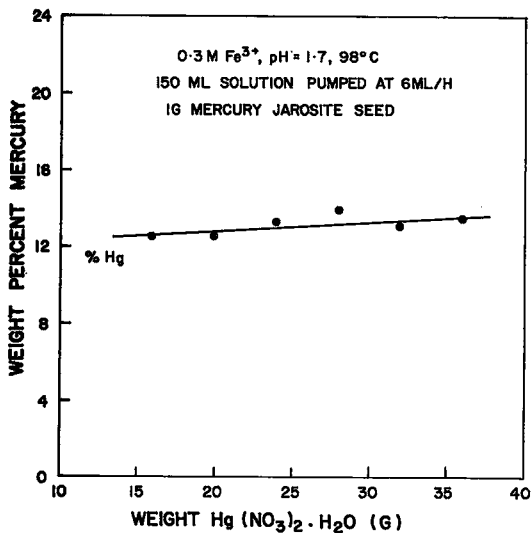

FIG. 5. The effect of the quantity of Hg^{2+} pumped into the hot Fe^{3+} solution on the mercury concentration of the product.

jarosite actually is $Hg_{0.5-x}(H_3O)_{2x}Fe_3(SO_4)_2(OH)_6$, where $2x$ is the amount of singly charged hydronium ion substituting for the doubly charged mercuric ion. The result of these factors is that all nitrate solutions pumped (Fig. 5) contained a stoichiometric excess of
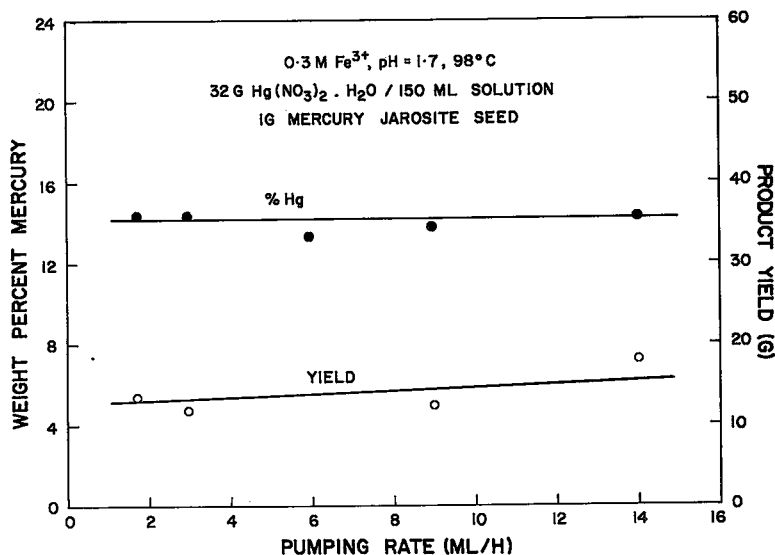
FIG. 6. The influence of the pumping rate of the mercuric nitrate solution on the yield and composition of the mercury jarosite.

mercury. Under such conditions, the mercury concentration in the product increased only slightly with increasing Hg^{2+} concentrations in solution.

Figure 6 illustrates the effect of the pumping rate on the mercury concentration and product yield. The mercury concentration of the jarosite-type compound is essentially independent of the pumping rate over the interval 2–14 ml *per* hour. The yield of product seems to increase slightly with increasing pumping rate, but the effect is not pronounced. When lead jarosite is made by the slow-addition method (Dutrizac *et al.* 1980), the pumping rate is a critical variable, probably because of the very low solubility of $PbSO_4$. All the tests were run for a minimum of 24 hours regardless of the total time required to pump the 150 ml of solution.

In order to assess the influence of reaction time on the formation of mercury jarosite, a series of experiments was conducted whereby a constant weight (32 g) of $Hg(NO_3)_2 \cdot H_2O$ was pumped at 6 ml *per* hour into a one-litre volume of 0.3 M Fe^{3+} solution. The effect of reaction time could be ascertained by varying the volume of nitrate solution. The results are summarized in Figure 7 for solution volumes ranging from 50 ml (8-hour reaction) to 350 ml (58-hour reaction). The results suggest a slight lowering of the mercury concentration with prolonged reaction times. Hydronium jarosite formation is known to be a slow process at 100°C; the longer reaction times presumably favor an in-

creased degree of hydronium ion substitution. The product yield is, within experimental accuracy, independent of the pumping time, and this observation is consistent with the observation that the reaction is controlled largely by pH, temperature and iron concentration once an excess of Hg^{2+} is available.

The mercury jarosite synthesis product

The optimum conditions identified for the synthesis of mercury jarosite by the slow-addition method are as follows: (1) 150 ml of solution containing 36 g $Hg(NO_3)_2 \cdot H_2O$ plus 4 ml concentrated HNO_3 (2) pumped at 6 ml *per* hour (3) into 1 l of 0.3 M Fe^{3+} (as SO_4) solution at pH = 1.7 at 98°C in a well-stirred baffled reactor with 2 g Hg-jarosite seed. The product is allowed to settle and the bulk of the liquid is decanted. The solids are then stirred for half an hour with one litre of cold (25°C) 0.3 M H_2SO_4 solution; the solids are allowed to settle and the liquid is decanted. This procedure is repeated three times. After the final acid wash, the charge is filtered, washed with 4 l hot water and then dried at 110°C in air. The mercury jarosite prepared under these conditions is a dull yellow color; the dullness is probably caused by the presence of traces of an unknown iron compound(s). The X-ray-diffraction pattern of the "pure" mercury jarosite is virtually identical to that reported previously (Dutrizac & Kaiman 1976). Figure 8
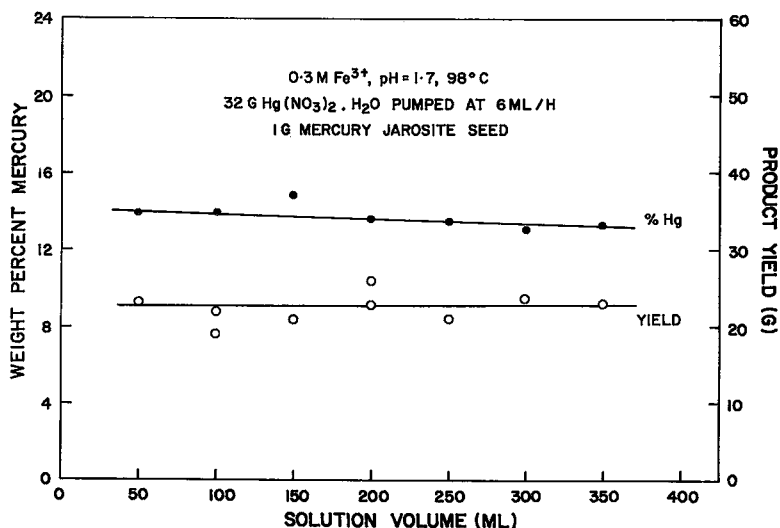
FIG. 7. Effect of the volume of the mercuric nitrate solution pumped, and hence of the pumping time, on the yield and composition of the mercury jarosite.

shows the morphology of the mercury jarosite product. The jarosite forms as pseudocubic rhombs up to 3 μm in width; the rhombs tend to be extensively intergrown, giving rise to larger aggregates that are in part responsible for the excellent settling and filtration properties of the jarosite family of compounds. The final product prepared under the preferred conditions has the composition given in Table 2.

Mercury–alkali jarosites

Mercury jarosites have not yet been found in nature. One possible explanation for the rarity of this compound is an unfavorable partition coefficient between ubiquitous alkalis such as K^+, Na^+ and Hg^{2+}: $[Hg/(Hg + K)]_{solution}/[Hg/(Hg + K)]_{solid}$. Such partition data are very useful to hydrometallurgists, since they permit the prediction of impurity distributions during jarosite formation under a wide range of conditions. To determine such distribution data for the K–Hg and Na–Hg systems, the following experiments were conducted. One litre of 0.3 M Fe^{3+} solution was prepared; 0.3 M Li_2SO_4 was added to ensure a copious supply of sulfate, and the pH was adjusted to 1.7; no seed was added. Then, 150 ml of solution containing various concentrations of $Hg(NO_3)_2$ and KNO_3 or $NaNO_3$ were pumped into the hot ferric sulfate medium, using the procedure described in the previous section. Figure 9 illustrates the distribution of Hg between the solution and the solid
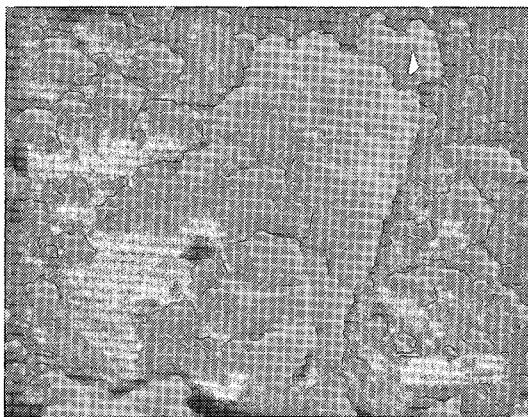

FIG. 8. SEM photomicrograph of the mercury jarosite synthesized under the preferred conditions.

phase in the Hg–K system. Clearly, potassium jarosite is favored over the corresponding mercury compound, and there is a strong tendency to incorporate potassium into the jarosite structure at the expense of mercury. The limiting partition coefficient for mercury precipitation from dilute Hg–K solutions is about 0.28 on a molar basis. On a simple weight basis, about 10% of the mercury present in the original solution is precipitated as jarosite from dilute solutions of mercury. Significantly, such a partition coefficient does not preclude at least a mer-

TABLE 2. COMPOSITION OF THE MERCURY JAROSITE PRODUCT

Element	This work	Dutrizac & Kaiman (1976)	Theoretical
Hg	13.74	14.62	17.85
Fe	30.31	35.65	34.19
SO$_4$	35.02	28.37	29.81
H$_3$O$^+$, OH$^-$	20.93	21.36	18.15
Formula	Hg$_{0.38}$(H$_3$O)$_{0.25}$	Hg$_{0.39}$(H$_3$O)$_{0.22}$	Hg$_{0.5}$Fe$_3$
	Fe$_{2.98}$(SO$_4$)$_2$(OH)$_6$	Fe$_{2.76}$(SO$_4$)$_2$(OH)$_6$	(SO$_4$)$_2$(OH)$_6$

curian jarosite in nature. Traces of potassium are effectively precipitated from Hg-rich solutions, and the partition coefficient K′ $\simeq$ 10 = [K/(K + Hg)]$_{solid}$/[K/(K + Hg)]$_{solution}$ under these conditions. Interestingly, even a trace amount of alkali in solution yields a jarosite-type product free of the unknown compound detected in all the simple mercury jarosites.

Figure 10 shows the corresponding partition data for the Na–Hg system realized under similar experimental conditions. In dilute Hg solutions, the mercury is precipitated in approximately the same ratio of Hg/(Hg + Na) as exists in solution; the partition coefficient is almost 0.9 on a molar basis. On a simple weight basis, about 18% of the mercury present in the original solution is precipitated as jarosite from Hg–Na solutions dilute in mercury. In mercury-rich solutions, however, the sodium is prefer-

entially concentrated into the jarosite-type phase with a partition coefficient for sodium of $\sim$7. The abrupt change in the shape of the liquid–solid partition curve may indicate a break in the properties of the Hg–Na jarosite solid-solution series, although this point was not pursued further in this study. These data certainly indicate that mercury would be readily incorporated into a jarosite-type compound from sodium–mercury solutions. An obvious conclusion arising from Figures 9 and 10 is that the lack (or scarcity) of natural mercurian jarosite is not caused by an extremely unfavorable M–Hg partition coefficient (e.g., $K < 10^{-3}$).

Other synthesis procedures

Other general synthesis procedures were employed to prepare mercury jarosite, but none was as successful as the slow-addition technique. The simplest procedure is to place the constituent sulfates in a vessel and heat to 100°C to form jarosite. This procedure is very effective for the alkali jarosites (Dutrizac & Kaiman 1976), but was found to be wholly ineffective for mercury jarosite.

Attempts to prepare mercury jarosite from sulfate media in an autoclave were somewhat more successful. Products containing 15–19% Hg
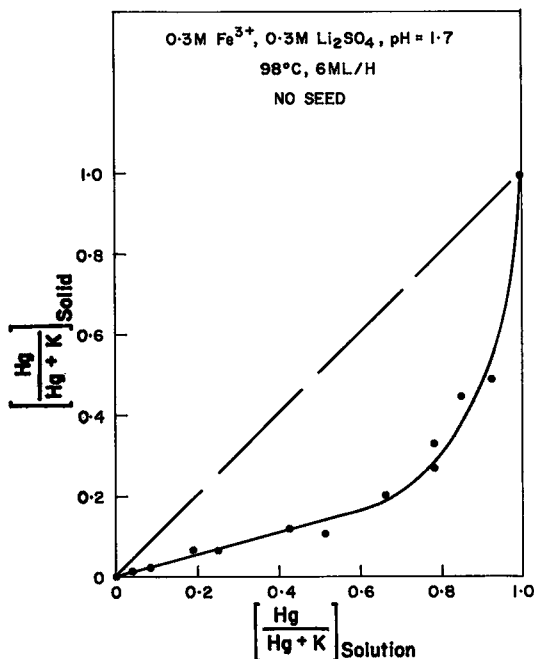

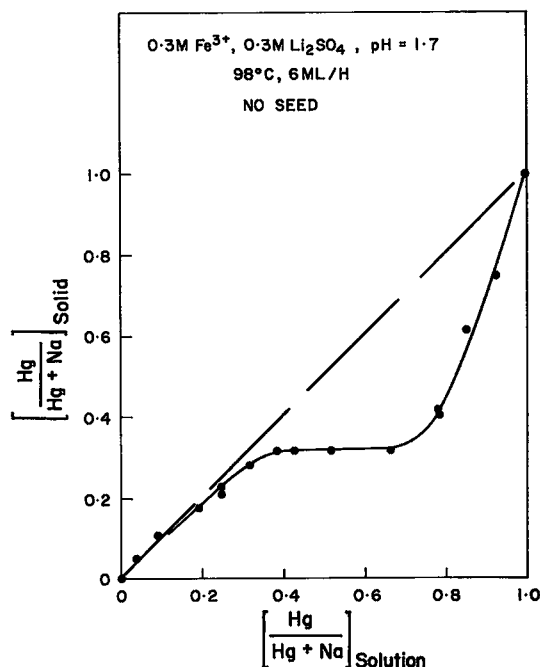FIG. 9. Solution-solid partition curve for jarosite formed from Hg^{2+}–K$^+$ media.

FIG. 10. Solution-solid partition curve for jarosite formed from Hg^{2+}–Na$^+$ media.

were produced, and these were shown to consist of mercury jarosite, trace to minor $HgSO_4 \cdot 2HgO$ and traces of the same unidentified iron compound found in the slow-addition synthesis experiments. Removal of the $HgSO_4 \cdot 2HgO$ impurity by acid washing yielded a 14–15% Hg material. This was possibly slightly richer in mercury than the slow-addition product, but the color was dark orange to brick red. Because the material was not significantly more mercury-rich than the slow-addition product and because part of the mercury could be associated with the colored iron compounds, the autoclave approach was not developed further. Additional development of the autoclave method might eventually yield a superior mercury jarosite.

Mercury jarosite in nature

So far as is known, mercury jarosite or even a significantly mercurian jarosite has not been reported as occurring naturally. Because jarosite-type compounds usually do not receive much detailed attention by mineralogists, commonly being studied only by X-ray diffraction and reported as "jarosite", it was felt desirable to analyze a number of natural jarosite-family minerals specifically for their mercury concentrations. Particular emphasis was placed on jarosite-family minerals from mercury deposits or from mercury-rich areas. The National Mineral Collection of the Geological Survey of Canada (GSC), the mineral collection of the Royal Ontario Museum (ROM) and the National Museum of Canada (NMC) were searched to locate jarosite-family minerals and, specifically, those intergrown with mercury minerals. Furthermore, additional samples were provided by the British Museum (Natural History) (BM) and by the U.S. National Museum of Natural History (USNM). Polished sections were prepared, and the jarosites were analyzed by the electron microprobe; where sufficient material was present in fair purity and where microscopic study showed the absence of mercury minerals, the specimens were also analyzed by wet-chemical techniques.

One sample from the Horse Heaven mine, Ashwood, Oregon (NMC 32250) consists of jarosite intergrown with cinnabar. Microscopic study of the jarosite indicated the presence of fine inclusions of cinnabar. Significantly, this sample gave no probe-detectable mercury (*i.e.,* less than 0.08% Hg). A second sample from Butte, Montana (NMC 32257), also consisting of jarosite intergrown with cinnabar, contains fine cinnabar inclusions in the jarosite itself. This sample also has less than the detection limit of
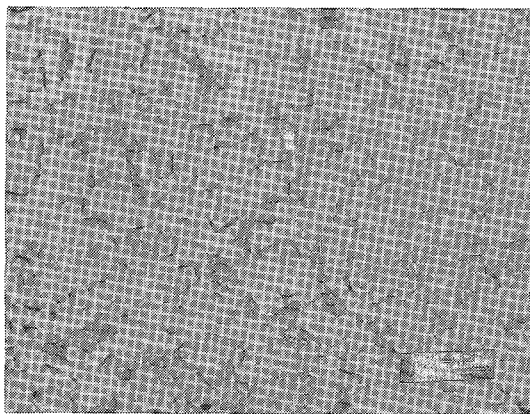

FIG. 11. SEM photomicrograph of jarosite with metacinnabar inclusions from Clausthal, West Germany. Crude grey crystals are jarosite, and white spots are HgS.

Hg. A specimen from Clausthal, West Germany (GSC 19295) consists of metacinnabar and jarosite; the jarosite is well crystallized and contains fine inclusions of metacinnabar (Fig. 11). This material was also probed; its jarosite also contains no detectable mercury (Hg < 0.08 wt. %).

The other jarosite-family minerals were also analyzed, and the results are presented in Table 3. For this work, the probe detection-limit for Hg was determined to be 0.08 wt. %. Significantly, none of the jarosite-family minerals studied contains any significant amounts of probe-detectable mercury, and none can even be described as "mercurian". Where accurate wet-chemical analyses were performed, the Hg concentrations were consistently <5 ppm. This finding, which is consistent with earlier analyses of jarosite-family compounds from mercury deposits (Novikova 1957, Zubov & Garbuz 1967, Razenkova & Samoilova 1972), indicates that mercury is not concentrated into a jarosite-type compound during the weathering of mercury sulfide deposits.
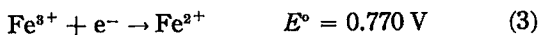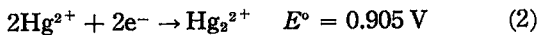
The above results show that mercury jarosite forms readily under suitable synthesis conditions. Although Figures 9 and 10 suggest that the partition of mercury in the presence of ubiquitous K or Na ions is not so unfavorable as to preclude at least a significantly mercurian jarosite, the prevalence of alkali ions in groundwater (Brown 1971) ensures that non-alkali jarosite-family minerals are relatively scarce and locally concentrated. Hence, the apparent total absence of mercury in jarosite-type compounds must be due to other factors; one of the most likely of

TABLE 3. MERCURY CONTENT OF SELECTED JAROSITE-FAMILY MINERALS

Source and museum number	Mineral	Probe analysis Hg (Wt.%)	Wet analysis Hg (ppm)
Horse Heaven mine, Ashwood, Oregon, NMC-32250	Jarosite	<0.08	----
Butte, Montana, NMC-32257	Jarosite	<0.08	----
Clausthal, West Germany, GSC-19295	Jarosite	<0.08	----
New Idria mine, California	Jarosite	<0.08	----
Terlingua, Texas, USNM-C-5236	Jarosite	<0.08	----
Nevada, ROM-M14306	Natrojarosite	----	<5
Utah, ROM-M13367	Argentojarosite	----	<5
France, ROM-M7097	Hydronium Jarosite	----	<5
Goodsprings, Nevada, ROM-M13464	Plumbojarosite	----	<5
Keno Hill, Yukon, ROM-M34513	Argentojarosite	----	<5
Tombstone, Arizona, ROM-M29589	Jarosite		
Chihuahua, Mexico, ROM-M15287	Plumbojarosite	----	<5
USSR, ROM-M23031	Jarosite	----	<5
New Mexico, ROM-M20884	Argentojarosite	----	<5
Chuquicamata, Chile, ROM-11188	Jarosite	----	<5
Esperanza mine, Almeria, Spain, BM-28172	Plumbojarosite	<0.08	----
Kamareza, Greece, BM-1972,210	Natrojarosite	<0.08	----
Charnay, France, BM-1906,236	Jarosite	<0.08	----
Limni, Cyprus, BM-67210	Natrojarosite	<0.08	----
Katanga, Zaire, BM-1949,61	Beaverite	0.08	----
Utah, USA, BM-1924,622	Argentojarosite	<0.08	----
Darwin mine, California	Jarosite	----	<5
Luning, Nevada	Natrojarosite	----	<5
Arsenic mine, Luning, Nevada, ROM-M16654	Jarosite	<0.08	----
Posokoni, Huanuni, Bolivia, ROM-M19860	Jarosite	<0.08	----
Otravara, Finland, ROM-M14574	Jarosite	<0.08	----
Antofagasta, Chile, ROM-M21523	Natrojarosite	<0.08	----

these is the effect of pH on jarosite precipitation. Of all the jarosite-type compounds studied, mercury jarosite is the most sensitive to pH. The compound does not form at all for pH <1.4, and at higher pH values the presence of other iron compounds or oxy-compounds of mercury predominates even in the slow-addition method. In most deposits, the mercury would probably hydrolyze to form Hg^{2+} oxy-minerals such as pinchite $Hg_5O_4Cl_2$, montroydite HgO, schuetteite $Hg_3(SO_4)O_2$, etc., before the kinetically slow process (at low temperatures) of jarosite formation occurs. Since other jarosite-family minerals can form over the pH range 1 to 3 (Brown 1971, Johnston 1977), the need for very close pH control to produce mercury jarosite would impose an additional constraint on the formation of this compound. An equally significant factor is that mercury jarosite can form only from Hg^{2+}, not from Hg^+. Very

strong oxidizing conditions are required to form Hg^{2+}, and such conditions may be limited even in the oxidation zones of sulfide deposits:

$$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+} \quad E^\circ = 0.905 \text{ V} \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^\circ = 0.770 \text{ V} \quad (3)$$

Various attempts were made to precipitate mercury from a chloride solution containing added Li_2SO_4 as the sulfate source, according to an established procedure (Dutrizac 1981). This technique yielded only small amounts of hydronium jarosite containing <0.5% Hg. The failure to precipitate mercury jarosite from a concentrated chloride solution is likely related to the formation of strong chloro-complexes. These cannot be accommodated in the jarosite structure for size–charge reasons, and give only a small equilibrium concentration of Hg^{2+} that is inadequate to form mercury jarosite. The complexation of mercury by chloride ion may be yet another factor hindering natural formation of mercury jarosite where chloride-rich solutions are commonly encountered.

The combination of the limited occurrence of Hg^{2+} with the ease of its hydrolysis is held responsible for the limited incorporation of Hg in natural jarosite-type compounds. The mercury hydrolysis problem is aggravated by the common association of mercury minerals with carbonates or other alkaline rocks that makes the establishment of strongly acidic (pH < 2) conditions difficult (Smirnov et al. 1976). Another factor that mitigates against mercury jarosite formation is the great resistance of cinnabar to chemical oxidation. Dissolved mercury concentrations tend to be low, and oxidation frequently does not occur until other sulfides such as pyrite have been leached away (Grdenić et al. 1978). The sulfides such as pyrite are responsible for the formation of acid and ferric ion, which are mandatory for jarosite formation; their removal before cinnabar oxidation would effectively preclude the incorporation of mercury in a jarosite-type compound. Although mercury jarosite or even a mercurian jarosite has not yet been found in nature and although many factors mitigate against their formation, such minerals may yet be discovered in the strongly oxidized portions of mercury sulfide deposits that contain ample pyrite for acid and iron generation and that show a relative lack of carbonates.

CONCLUSIONS

Of the techniques available for the synthesis of mercury jarosite, the slow-addition method seems most promising for making either pure

mercury jarosite or alkali–mercury jarosites. The most critical factor associated with the slow-addition method is the pH of the hot iron sulfate solution, which must be regulated: 1.4 < pH < 2.0. High temperatures are necessary for adequate product yields, but the Hg content is relatively temperature-independent. The product yield depends directly on the iron concentration, but the jarosite composition is only slightly affected by this variable. Once above-stoichiometric quantities of the Hg^{2+} ion are pumped, the yield and jarosite concentration become nearly independent of the amount of mercury, the total pumping time (solution volume) and the pumping rate. The mercury partition coefficients for the Hg–K and Hg–Na systems were determined. In the Hg–K system, potassium is preferentially precipitated as jarosite, and the limiting molar partition coefficient for mercury in dilute media is 0.28. By contrast, dilute mercury solutions in the Hg–Na system behave nearly ideally, and the limiting partition coefficient is 0.9.

Several jarosite-family minerals were analyzed for mercury, but none contains significant concentrations (> 0.08 wt. % Hg) of this element. Jarosite intergrown with cinnabar is likewise essentially mercury free. Reasons for the absence of a mercury-rich jarosite include the ease of hydrolysis of the Hg^{2+} ion, the high oxidation potential of Hg^{2+} and the resistance of cinnabar to chemical weathering.

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