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Precipitation of Jarosite-Type Double Salts from Spent Acid Solutions from a Chemical Coal Cleaning Process

by

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ABSTRACT

The precipitation of jarosite compounds to remove Na, K, Fe, and SO_4^{2-} impurities from spent acid solutions from a chemical coal cleaning process was studied. Simple heating of model solutions containing $Fe_2(SO_4)_3$, Na_2SO_4, and K_2SO_4 caused jarosite ($KFe_3(SO_4)_2(OH)_6$) to form preferentially to natrojarosite ($NaFe_3(SO_4)_2(OH)_6$). Virtually all of the K, about 90% of the Fe, and about 30% of the SO_4^{2-} could be precipitated from those solutions at 95°C, while little or no Na was removed. However, simple heating of model solutions containing only $Fe_2(SO_4)_3$ and Na_2SO_4 up to 95°C for $\leq$12 hours produced low yields of jarosite compounds, and the Fe concentration in the solution had to be increased to avoid the formation of undesirable Fe compounds.

Precipitate yields could be increased dramatically in model solutions of $Na_2SO_4/Fe_2(SO_4)_3$ containing excess Fe by using either $CaCO_3$, $Ca(OH)_2$, or ZnO to neutralize H_2SO_4 released during hydrolysis of the $Fe_2(SO_4)_3$ and during the precipitation reactions. When $CaCO_3$ was used, the precipitate consisted of natrojarosite and gypsum ($CaSO_4 \cdot 2H_2O$). Although Fe and SO_4^{2-} could be removed effectively at pH values of 1.5-2.3, optimum Na removal was possible only within the pH range of 1.4-1.6. Maximum precipitate yields were obtained within 6 hours at both 80 and 95°C, with at least 80% of the Fe and SO_4^{2-} and about 60-75% of the Na removed. Complete removal of Na in those tests was probably precluded by hydronium ion substitution for the Na.

The results obtained from the studies with model solutions were applied to spent acids produced during laboratory countercurrent washing of coal which had been leached with a molten NaOH/KOH mixture. Results indicated that jarosite compounds can be precipitated effectively from spent acid solutions by heating for 6 hours at 80°C while maintaining a pH of about 1.5 using $CaCO_3$.

GENERAL INTRODUCTION

Emissions of sulfur and ash during coal combustion are known to be deleterious to the environment and therefore are controlled by state and federal regulatory requirements. One method for reducing emissions of sulfur oxides and ash produced by coal combustion is to remove sulfur and mineral matter from coal prior to combustion using physical coal cleaning methods such as cyclones, jigs, or concentrating tables. However, physical cleaning methods are not effective for removing the organic portion of the sulfur or fine disseminated mineral grains in the organic matrix.

Although coal can contain as much as 10 wt. % sulfur, the total sulfur content of most coals is between 1.0 and 4.0 wt. % (1). The organic sulfur fraction typically comprises 30-70% of the total sulfur (2). Because conventional physical cleaning methods can not remove the organic sulfur and can remove only a portion of the inorganic sulfur, these methods typically remove only 10-35% of the total sulfur in coal (3). To reduce further the sulfur content of the coal, chemical cleaning techniques are required in addition to physical cleaning techniques. While chemical cleaning is often superior to physical cleaning in its ability to remove sulfur and mineral matter, the development of chemical cleaning methods has been slow because they are expensive relative to physical cleaning techniques (4). Typical costs for physical cleaning methods range from $3-12/ton of feed coal, while costs associated with chemical cleaning methods are on the order of $40/ton (5).

One promising approach for chemically cleaning coal is to use molten NaOH or a mixture of NaOH plus KOH as leaching agents and then wash the leached coal with hot water and dilute H_2SO_4. The first water wash removes most of the caustic (NaOH, KOH, or both) and the coal-derived Al, S, and Si, while the wash with H_2SO_4 removes residual caustic and the coal-derived Fe (6). The final water wash removes the H_2SO_4 from the coal. This process effectively removes both inorganic and organic sulfur as well as ash from coal.

The initial water wash alone might typically consist of four weights of water per weight of coal (6). In order to improve the economics of the process, it is necessary to optimize the quantities of chemicals and volumes of wash water used during chemical coal cleaning. One approach for reducing operating costs is to treat the spent acid so it can be recycled back into the system. The spent H_2SO_4 contains substantial amounts of Na, K, and Fe impurities which must be removed prior to being recycled to the acid washing step for cleaning additional coal. Ideally, the spent acid treatment should be capable of transforming impurities from soluble to solid form and produce precipitate sludges that have potential for recovery of impurities and do not pose environmental problems. Substantial amounts of impurities can be removed by precipitating jarosite compounds which are double salts of Na (or Na plus K) and Fe. Jarosite compounds have the general formula $MFe_3(SO_4)_2(OH)_6$, where "M" is a monovalent cation such as Na or K.

A useful characteristic of jarosite compounds is their stability and low leaching potential. From a theoretical standpoint, precipitation of jarosite compounds from spent acid solutions is kinetically and thermodynamically feasible. However, the technical feasibility of this treatment approach for coal cleaning wastewater needs to be investigated.

Research Objectives

After reviewing the pertinent literature on precipitation of jarosite compounds, it was evident that experimental work was needed to determine whether this approach to treating the spent acid was suitable. Thus, experiments were performed to help evaluate the applicability of this approach. The research objectives were: to determine whether precipitation of jarosite compounds from spent acid solutions is technically feasible; to identify the important reaction parameters for effectively precipitating these compounds; and to ascertain the effectiveness of this acid treatment approach in removing the impurities. With regard to the later objective, the removal of alkali metals was of particular interest, since the iron and sulfate can be easily removed by liming the acid.

Experimental Approach

In order to meet these objectives, the effects of reaction time, temperature, and pH on the effectiveness of precipitating jarosite compounds from model spent acid solutions was studied. In addition to using the model solutions, a precipitation experiment was performed using spent acid obtained from simulated countercurrent washing of caustic-treated coal. The effectiveness of the precipitation experiments in removing impurities was determined by obtaining precipitate yields, by performing chemical and mineralogical analyses on the precipitates, and by performing chemical analyses on the final solutions after filtering the precipitates. Quantifying the magnitude of impurity removal enabled an assessment of the feasibility of using this treatment approach to be made. If substantial reductions in levels of impurities were not obtained, other environmentally acceptable approaches to the problem would need to be proposed and evaluated.

Explanation of Thesis Format

The thesis is written in an alternate format and consists of a literature review and two manuscripts which have been submitted to scientific journals for publication. The literature review summarizes available literature on precipitation of jarosite compounds from acidic process or waste streams. Discussions on atomic substitutions in the crystal lattice, synthesis conditions, kinetics, thermodynamics, and reaction chemistry are included in the review. The first manuscript, entitled "Precipitation of Iron, Sodium, and Potassium Impurities from Synthetic Solutions Modeling Spent Acid Streams from a Chemical Coal Cleaning Process," was submitted to Fuel Science and Technology International and deals predominantly with research on precipitating jarosite compounds by heating solutions modeling spent acid solutions from the chemical coal cleaning process without maintaining specific pH values during the precipitation. The effects of reaction time, temperature, and starting pH of the solution are discussed.

The second paper, entitled "Precipitation of Jarosite Compounds as a Method for Removing Impurities from Acidic Wastes from Chemical Coal

Cleaning," was submitted to Environmental Science and Technology and deals primarily with precipitation of jarosite compounds from acid solutions while maintaining specific pH values by using a neutralizing agent. This paper discusses the effects of pH (maintained during precipitation by neutralizing the acid formed during precipitation with a neutralizing agent) and reaction time on the removal of Na, Fe, and SO_4^{2-} impurities.

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LITERATURE REVIEW ON JAROSITE COMPOUNDS

Introduction

Jarosite-type compounds form when sulfides undergo strong oxidation under highly acidic (pH <3) conditions (1). The jarosite family of compounds has the theoretical formula $MFe_3(SO_4)_2(OH)_6$, where "M" is a monovalent cation from the group H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, Tl^+, $1/2Pb^{2+}$, or $1/2Hg^{2+}$ (2,3). All but the Rb, Tl, and Hg species occur naturally (4). The natural compounds are named according to the predominant "M" ion. The members of the jarosite family of compounds are typically yellow to dark brown in color (5). Chemical and mineral names of jarosite compounds are listed in Table 1 below. Natural jarosite compounds are composed primarily of the Na, K, and H_3O species (2,4). Jarosite is much more prevalent than natrojarosite, and the occurrence of relatively pure hydronium jarosite is rare (6). Some typical representations of the jarosite structure are shown in Figure 1.

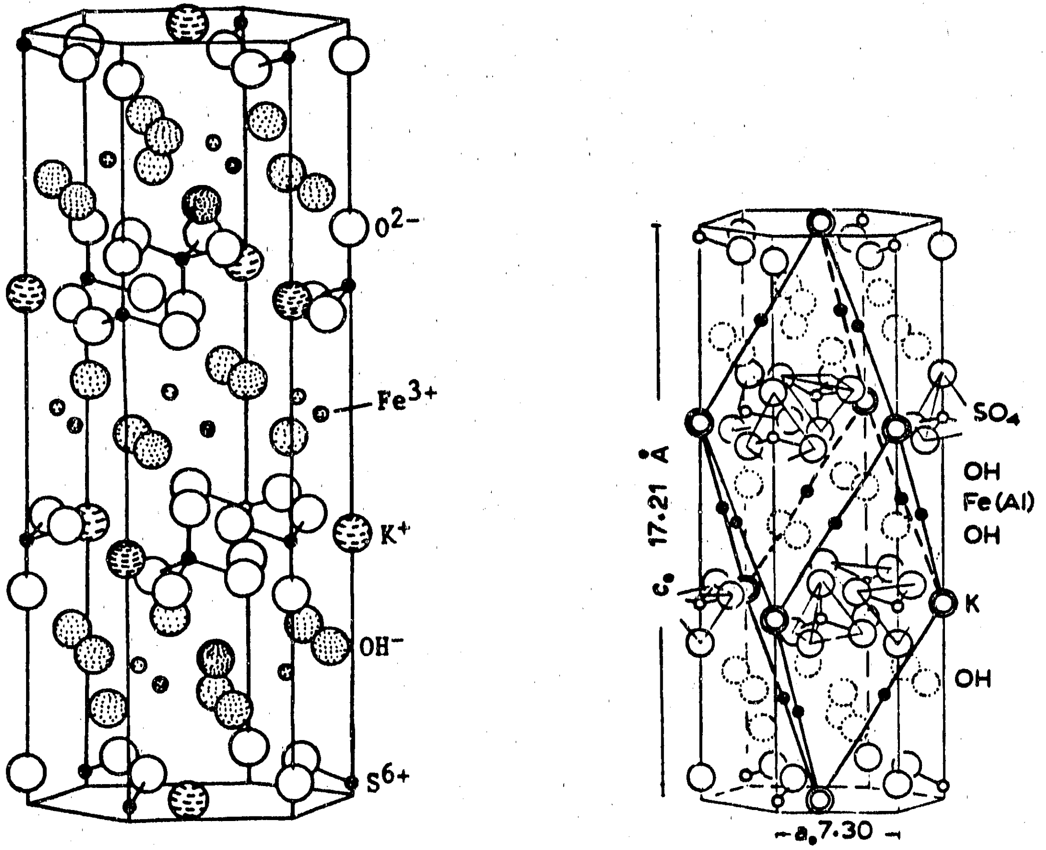
Confusion can arise when the term "jarosite" is used, since it can refer to either the K-bearing jarosite species or the jarosite family of compounds as a whole. In this paper, "jarosite compounds" will denote the jarosite family, while "jarosite" will refer to only the K-bearing mineral species.

The precipitation of jarosite compounds is one potential method for removing unwanted iron, sulfate, or alkali metal ions from chemical wastes or from chemical process streams. In the following sections, the

Table 1. Chemical and mineral names of jarosite compounds[a]

Formula	Chemical Name	Mineral Name
$AgFe_3(SO_4)_2(OH)_6$	silver jarosite	argentojarosite
$(H_3O)Fe_3(SO_4)_2(OH)_6$	hydronium jarosite	hydronium jarosite
$Hg_{0.5}Fe_3(SO_4)_2(OH)_6$	mercury jarosite	none
$KFe_3(SO_4)_2(OH)_6$	potassium jarosite	jarosite
$NaFe_3(SO_4)_2(OH)_6$	sodium jarosite	natrojarosite
$(NH_4)Fe_3(SO_4)_2(OH)_6$	ammonium jarosite	ammoniojarosite
$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$	lead jarosite	plumbojarosite
$RbFe_3(SO_4)_2(OH)_6$	rubidium jarosite	none
$TlFe_3(SO_4)_2(OH)_6$	thallium jarosite	none

[a] From reference 4.



Cited from ref. 7

Cited from ref. 8

Figure 1. Typical representations of the jarosite structure

synthesis of jarosite compounds is discussed. In addition, separate sections on atomic substitutions in jarosite compounds and on the kinetics and thermodynamics associated with precipitating these species are included. Because jarosite, natrojarosite, and hydronium jarosite are the compounds of primary importance to this work, formation of other jarosite species is not reviewed.

Synthesis of Jarosite Compounds

Literature related to precipitating jarosite compounds can be divided into three broad categories. These are: 1) patents on double salt precipitation from industrial waste streams, 2) discussions of the Jarosite Process used in hydrometallurgical processing, and 3) laboratory synthesis of jarosite compounds. Each category is discussed separately below.

Patents

The precipitation of double salts from various industrial waste and process streams is discussed in a number of patents (see Table 2 on page 19 for summary of reaction conditions). In a patent pertaining to hydrometallurgical processing of Zn-rich solutions, Fe is precipitated at atmospheric pressure in the presence of K, Na, or NH_4 ions as a basic iron sulfate with good decanting and filtering properties (9). Reaction times are 3-4 hours, the preferred reaction temperature is about 95°C, and the maximum pH is 1.5. A neutralizing agent, such as ZnO, is used to obtain the desired pH. However, ferric hydroxide can precipitate instead of basic iron sulfates if the ZnO is added too quickly (10).

The patent states that the "M" ion concentration should be 1/10 to 1/4 of the Fe concentration in g/L (9).

In another patent, natrojarosite is precipitated as part of a hydrometallurgical process in which cobalt is recovered after leaching cobaltite-pyrite concentrates under pressure with NaCl or Na_2SO_4 solutions at 130-160°C in an autoclave (11). The leach slurry from the autoclave is discharged and natrojarosite is precipitated by neutralizing the slurry to a pH value of 1.0-1.5 with lime, limestone, or another neutralizing agent, and heating the slurry at 85-95°C at ambient pressure.

Three similar patents by the same inventors describe precipitation of insoluble basic sodium hydroxy ferric sulfates from various industrial sodium sulfate wastes, including wastes in process feedwater demineralizers, power plant cooling tower blowdown sludge, and alkali-based scrubbers used for flue gas desulfurization (12-14). These wastes can be reacted with iron and H_2SO_4 to form insoluble co-precipitated double salts of ferric sulfate and sodium sulfate. The primary insoluble sulfate double salts are very similar to the minerals natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), sideronatrite ($Na_2Fe(SO_4)_2OH \cdot 3H_2O$), and metasideronatrite ($Na_4Fe_2(SO_4)_4(OH)_2 \cdot 3H_2O$). The patents state that these compounds are 1000 to 10,000 times less soluble than the initial waste streams and are generally 10 to 100 times less soluble than $CaSO_4$, the end product of many flue gas desulfurization systems. The solubility of natrojarosite at room temperature is 0.02 to 0.4 g/L, depending if the measurement method is based on Na or Fe determination (12-14). The solubilities obtained by determining Fe (lower of the two values) were considered to be more accurate. Because of the low aqueous solubilities of the precipitates, the patents state that these materials can be disposed of in a landfill without posing water pollution hazards. Another potential use for these double salts is as roadfill or as aggregate for concrete (14). In addition to being relatively water-insoluble, the double salts are crystalline and can be easily dewatered and dried.

The overall stoichiometry for producing natrojarosite can be expressed in simplified form by the following reaction (14):

$$3Fe_2(SO_4)_3 + Na_2SO_4 + 12H_2O \longrightarrow 2NaFe_3(SO_4)_2(OH)_6 + 6H_2SO_4$$

Thus, it can be seen that acid is liberated during the precipitation of natrojarosite, thereby decreasing the pH of the solution as the reaction progresses.

Although the Fe must be in the ferric state in order to form the desired sulfate double salts, elemental or ferrous iron can be converted to the trivalent state by air oxidation or bacterial activation (13). The patents state that the ferric ion concentration should initially be at least 4 g/L. Excess oxygen and alkalinity should be avoided to minimize oxidation of the Fe to iron hydroxide compounds such as $Fe(OH)_2$, $Fe(OH)_3$, or FeOOH, which are water-insoluble gelatinous precipiates that are difficult to separate, dewater, and dry (12). In cases where it is desirable to increase the iron content, ferric sulfate can be added as either a solution or dry compound. Other metal cations, including Ag, Cu, Pb, and Zn, do not interfere with the formation of natrojarosite and can be co-precipitated (12-14).

For precipitating the double salts, ambient pressure is preferred, although sub- or super-atmospheric pressures can also be used. The effect of pressure on the precipitation reactions was not discussed. The reaction times stated in the patents were given in vague terms such as between "1 second and 7 days" (13). The preferred temperature for abiotic operation is between 120-180°F and most preferably between 130-150°F (13). The end products are at least partially dependent on pH. The patents state that natrojarosite may be produced below a pH of about 4, with a preferred pH range of 1.8 to 2.5 for natrojarosite (14). However, it is not stated whether these are initial pH values or actual pH values measured during precipitation.

A variety of conditions for precipitation of double salts are tabulated in two of the patents. The tabulated conditions include ion concentrations, Na:Fe mole ratios, pH, and the mineralogical composition of the precipitate (13,14). It is stated that "good yield" is obtained using the described conditions "at temperatures on the order of below about 130°F". However, "good yield" is not clarified and the "described conditions" are vague. Exact temperatures, reaction times, and yields are not given, and even though pH values are provided, the reported pH value could be the initial, final, or constant pH (using acid neutralization). Also, it is not clear whether the listed compounds were the only ones precipitated.

Seeding with natrojarosite can allow this double salt to be produced under conditions where the precipitation of iron hydroxides would normally be expected to predominate. For example, seeding a low-pH solution followed by increasing the pH to a "higher range" can precipitate the double salts of interest without significant amounts of the iron hydroxides being formed (14).

The Jarosite Process

In the hydrometallurgical processing of Zn, roasted Zn ore is leached with a hot H_2SO_4 solution and the Zn is recovered subsequently by an electrolytic process. At most Zn plants, Fe impurities in the hot acid leach solutions are removed by either the Jarosite Process or Goethite Process prior to electrolysis (15). The Jarosite Process is the most commonly used method for removing Fe impurities from the Zn leach liquors (3,16), and is also applicable to hydrometallurgical operations used in the processing of other metals, including Cu, Co, and Mn (17).

The Jarosite Process consists of adding a source of a monovalent cation, such as Na^+, K^+, or NH_4^+, to the acidic leach solution to precipitate Fe as a basic ferric sulfate in the jarosite group of minerals by heating the leach solution at 95°C at a pH value of 1.5 (3,15). Precipitation is continued until the Fe concentration is lowered from about 20 g/L to about 1 g/L, and the residual Fe is used to precipitate ferric hydroxide and scavenge other impurities (3). Reaction times for the precipitation are not given. Although jarosite is less soluble than natrojarosite or ammoniojarosite at a given pH, Na^+ or NH_4^+ are often used in the Jarosite Process since they are less expensive than K^+ (18). Typically, the NH_4^+ is added as aqueous ammonia. If Na is used, it can be either in the form of a hydroxide or sulfate (15). However, strong alkalis such as NaOH are used primarily in scavenging operations to form gelatinous, voluminous, flocculated colloids, but are not usually good precipitating agents for metal hydroxides since the pH is hard to control, even for dilute alkali solutions (16).

The Jarosite Process is flexible, can be easily adapted to existing operations, operates at less than 100°C and atmospheric pressure, has a high degree of Fe removal, and operates in acidic solutions, thereby saving on neutralization costs (3,17). Although the process can operate at temperatures of greater than 100°C, lower temperatures are preferred due to economic considerations. The precipitate settles rapidly (2) and is easily filtered and washed (17). The effect of seeding with a particular jarosite compound to enhance the precipitation of that species is not clear, and it is uncertain whether seeding is even necessary (19).

Disadvantages to the Jarosite Process include the need to add a precipitating reagent and the substantial amounts of residue formed (3). For a typical Zn ore, it has been estimated that about 0.5 tons (short tons or long tons not specified) of jarosite compounds are precipitated for each ton of Zn produced (3).

The overall reaction for precipitating natrojarosite (see previous section) is complex because isomorphic substitutions occur for the alkali metal (18). In addition, the reaction pathways for precipitating a given jarosite-type compound are not well understood (19). The chemical reactions have been summarized as follows for natrojarosite (20):

1) $3Fe_2(SO_4)_3 + 6H_2O \longrightarrow 6Fe(OH)SO_4 + 3H_2SO_4$

2) $4Fe(OH)SO_4 + 4H_2O \longrightarrow 2Fe_2(OH)_4SO_4 + 2H_2SO_4$

3) $2Fe(OH)SO_4 + 2Fe_2(OH)_4SO_4 + Na_2SO_4 + 2H_2O \longrightarrow$
$Na_2Fe_6(SO_4)_4(OH)_{12} + 6H_2SO_4$

4) $2Fe(OH)SO_4 + 2Fe_2(OH)_4SO_4 + 4H_2O \longrightarrow (H_3O)_2Fe_6(SO_4)_4(OH)_{12} +$
$5H_2SO_4$

The authors state that the hydrolysis taking place in reactions 1 and 2 is slow and requires an initial reaction period (unspecified) to initiate the reaction chain. It should be noted that reaction 3 is not balanced as written, but would be balanced if only one mole of H_2SO_4 is produced. Similarly, reaction 4 is not balanced as shown, but would be balanced if no H_2SO_4 is produced.

A neutralizing agent must be added to react with part of the free acid in solution and to neutralize the acid liberated during hydrolysis so that the reactions can go to completion (15,20). For this purpose, calcine (roasted Zn sulfide ore) is added to maintain the desired pH and the reaction is performed at about 95°C at a pH of about 1.5 (3,16,18). There is a critical minimum pH where the formation of jarosite compounds is suppressed, which is about 0.5 for natrojarosite (17). It is unclear whether this is an initial pH or the pH during actual precipitation. One source states that the temperature and pH are probably the two most important control variables and that the pH must remain below about 1.8 in order to prevent the precipitation of other Fe phases (19). Another source states that near optimum conditions for synthesis of jarosite compounds are 0.1 M Fe^{+3}, 0.01 M H_2SO_4, 100g/L M^{2+} as M_2SO_4, 97°C, 24 hours, and good agitation in air (17). Good agitation helps ensure rapid mixing of the reactants, promotes crystal growth, and keeps the precipitate in suspension (18). No information was found in the literature on the effects of the degree of agitation on the yield or composition of jarosite or natrojarosite.

The extent of Fe precipitation as alkali jarosite compounds increases with temperature, alkali ion concentration, and pH (18). Thus, a high temperature can theoretically compensate for acidic conditions. For example, the same degree of iron removal can be obtained at 180°C with 40 g/L H_2SO_4 as at 95°C with 5 g/L H_2SO_4 (19). The rate of Fe precipitation also increases as the Fe concentration increases, but the rate appears to be independent of the alkali concentration once the stoichiometric amount of alkali metal is present (18,19).

Impurities of environmental concern, such as As, Cd, and Pb, can also be removed during precipitation, although it is not clear whether these impurities precipitate as separate mineral phases. The precipitation of these impurities is variable and depends on numerous factors, including pH, kinds of impurities and respective concentrations, completeness of Fe removal, and the crystallinity and particle size of the precipitate (18).

Laboratory synthesis

Alkali jarosite compounds have been synthesized in the laboratory using a variety of procedures and reaction conditions. In one method, jarosite was formed at temperatures of 20-200°C in the pH range of 1 to 3 by adding KOH to ferric sulfate solutions (21). In another case, alkali jarosite compounds were synthesized at temperatures of 100-200°C by using solutions of ferric sulfate and alkali hydroxides (22). A more common method of synthesizing alkali jarosite compounds is by reacting acidic aqueous solutions of iron sulfates and alkali sulfates. In many studies, the pH of the solution was not controlled during the precipitation. However, the starting pH of the solution often was adjusted to a specific value. Although jarosite forms preferentially to hydronium jarosite, pure hydronium jarosite can be synthesized in the absence of alkali at temperatures of 25-170°C (23).

In one study, jarosite was precipitated from an acidic aqueous solution of K_2SO_4 and $Fe_2(SO_4)_3$ (24). The mixture was heated in a sealed tube at 110°C for 24 hours and then for an additional 24 hours at 165-180°C. It was noted that increasing the temperature above 110°C can increase the yield by promoting more rapid hydrolysis of the iron salt. This may be related to an increase in the reaction rate associated with the effective increase in concentration due to the pressure at temperatures greater than 110°C. When temperatures were as low as 90°C, basic sulfates of Fe and K which contained twice as much water and less alkali metal were produced.

In another study, natrojarosite/hydronium jarosite was precipitated at a pH of < 1.7 at 90-100°C (25). Colloidal $Fe(OH)_3$ formed at a pH of

>1.8. The ratio of natrojarosite to hydronium jarosite increased with temperature. The temperature range was not specified in the abstract cited for that study.

In other tests, potassium and sodium jarosites were precipitated in several hours by heating an acidic $Fe_2(SO_4)_3$ solution with alkali sulfates in water to near the boiling point or at temperatures of >100°C in an autoclave or an oil bath (4,6,17,22). In one study, addition of varying amounts of Na_2SO_4 increased both the precipitate yield and the Na content of the natrojarosite until the stoichiometric amount of Na theoretically necessary for complete iron removal as natrojarosite was reached (17). Then, the precipitate yield and Na content of the precipitate remained constant even with further increases in the Na_2SO_4 concentration.

Natrojarosite has also been produced in chloride-rich solutions at 95-100°C (26). Sulfate concentration and initial pH were the critical factors affecting jarosite precipitation from chloride media.

Another source of jarosite compounds is of Fe and alkali sulfate solutions at about 25°C and at atmospheric pressure, but reaction times were on the order of months to years (23,27,28). In one study, increasing the initial pH values by less than one pH unit caused the reactions to occur with "greater intensity" (28).

Summary of synthesis conditions

A brief summary of some of the conditions used to synthesize jarosite compounds is shown in Table 2. This table is not meant to represent an exhaustive summary of the literature. Rather, it is

Table 2. Synthesis conditions for jarosite compounds

Time (Hrs)	Temp. (°C)	pH	Grams/Liter			Fe:Na/K Molar Ratio	Refs. Cited
			Fe	Na + K	SO_4		
Jarosite Process							
4	95	1.5[a]	20-35	2-8	NG[b]	1-7	9[c]
NG[b]	95	1.5[a]	20	NG[b]	NG[b]	---	3
NG[b]	90-95	1.3-1.5[a]	25-30	NG[b]	NG[b]	---	18
Laboratory Synthesis							
670-4000	25	0.8-2.1[d]	3.3-33	0.8-8	7.6-76	3	23
10,100	25	2.1-3.2[d]	0.7-0.9	0.08	0.8-2.1	1-8	28
72	90-110	<1.5	17	2-4	5	3	6
NG[b]	90-110	<1.7	NG[b]	NG[b]	NG[b]	NG[b]	25
1.5-3	95	~1.7	10	20	70	0.2	4
24	95	0.5-1.9[d]	17	2-14	NG[b]	0.6-4	17
4	95-210	NG[b]	24-48	0.4-30	60-150	1-94	22[e]
48	110-180	<1.5	22	4	63	4	24[e]
Misc. Patents							
<72	<55	1.8-2.2	4.6-9.3	3.9-10	28-32	0.2-1	12-14
NG[b]	85-95	1.0-1.5[a]	$\geq$35	6.5	NG[b]	>2	11

[a] Maintained with a neutralizing agent.

[b] NG - Not Given.

[c] Unspecified basic sulfate formed.

[d] Initial pH of solution.

[e] Performed at greater than atmospheric pressure.

intended to show examples of some of the conditions used to synthesize alkali jarosite compounds. For the Jarosite Process, concentrations of an alkali metal were generally not provided since ammonium was used as the precipitating agent in most cases. However, entries were still made in the table for the Jarosite Process since the reaction conditions are pertinent to the formation of sodium and potassium jarosite as well. It should be noted that some of the references cited presented only typical reaction conditions (e.g., for the Jarosite Process) and contained no discussions of specific synthesis experiments.

There were numerous variations in experimental setups among the studies. Reaction parameters of time, temperature, iron and alkali metal concentrations, and pH varied considerably among the studies. Some of the experimental variables used in the studies included the initial oxidation state of the Fe, the hydration state of the $Fe_2(SO_4)_3$ (often not specified), and the presence of other inorganic species (e.g., Cl) in the precipitating solution. Also, the precipitate yields were often not given and it was not stated whether the reported pH value was an initial, final, or constant (using a neutralizing agent) pH.

Reported reaction times can be ambiguous, since the degree of completion is not specified. Reaction times may be misleading if, for example, reaction times of 48 hours were used but reactions were completed within only 4 hours. However, some useful information can be extracted from these data. When reaction times were on the order of weeks to months, the reaction temperature was only about 25°C. Concentrations of Fe and alkali metal ranged from <1 g/L to more than 30 g/L, and the mole ratios of Fe to the alkali metal also varied widely.

However, since precipitate yields were often not given, the effectiveness of each set of reaction conditions is difficult to deduce.

Atomic Substitutions

Contradictory statements have been made in the literature regarding the co-precipitation of divalent cations (e.g., Cd, Cu, Ni, Pb, and Zn) with jarosite compounds by substituting for the ferric iron. Variations in reaction conditions and solution compositions among studies may be responsible for conflicting reports. A slight deficiency in Fe concentrations relative to sulfate is common for alkali jarosite compounds (4). In one study, divalent base metals, including Cu^{+2} and Zn^{+2}, apparently substituted for the Fe^{+3} (17). This substitution leaves a charge imbalance, and how the charge requirements are satisfied is unclear. In the report, the author speculated that the charge requirements are achieved by an OH^- group combining with a proton in the solution to form water. It is uncertain whether this water remains in the crystal. The extent of divalent base metal incorporation into alkali jarosite compounds appears to be less than 3 wt. % (17). These low concentrations preclude obtaining direct crystallographic proof for the substitution of divalent metals for the Fe^{+3}. As the pH increases, the divalent base metals are hydrolyzed more extensively and can be incorporated more readily into the crystal lattice (17). Jarosite incorporates divalent base metals to a greater extent than natrojarosite.

Trivalent ions, including Al^{+3}, can also substitute for the ferric iron in alkali jarosites. This substitution is favored by high temperatures and lower acid conditions (17), although the Al substitution usually occurs in small amounts (5,29).

A wide range of ionic radii are possible in the "M" position, which is attributed to the relative openness of the structure (29). Hydronium ion substitution for the "M" ion in jarosite compounds has received a substantial amount of attention. Most researchers report a deficiency of Na and K ions in synthetic alkali jarosites under all synthesis conditions (4,22). The deficiency of alkali in jarosites is usually accompanied by excess water (includes H_2O and H_3O^+) (6,30), which is generally determined by difference. This excess water contracts the unit cell of jarosite and expands the natrojarosite unit cell (22). The authors speculated that this may be partially attributable to the fact that the ionic radius of H_3O^+ is larger than that of Na^+ but smaller than that of K^+. NMR and IR absorption spectroscopy have shown that the excess water is due to H_3O^+ in the lattice structure (30). Thus, although the theoretical composition of jarosite compounds is $MFe_3(SO_4)_2(OH)_6$, the actual composition for most natural and synthetic jarosite compounds is $M_{(1-x)}(H_3O)_xFe_3(SO_4)_2(OH)_6$ where "x" is typically 0.15 to 0.25 (17).

The degree of H_3O^+ substitution in natrojarosite is more extensive than in jarosite (31). Because of the H_3O^+ substitution, the consumption of NH_4^+ in the Jarosite Process is usually 80% or less of the theoretical consumption (3). The extent of H_3O^+ substitution is probably dependent on the formation conditions (2,4). Some of the primary factors affecting M-site occupancy and product yield are temperature, pH, time, and concentrations of Fe and "M" ions (17).

In one study, the pH of the solution was initially adjusted to specific values prior to heating; no other pH adjustments were performed. The Na content of natrojarosite was not significantly affected by the initial room temperature pH in the range of 0.7-1.9 under the conditions studied (0.3M Fe^{+3}, 0.3M Na_2SO_4, 1.0M $ZnSO_4$, 97°C, 24 hours) (17). Although this seemingly might imply that H_3O^+ substitution was independent of pH under these conditions, it must be kept in mind that these are only initial room temperature pH values, and the actual pH values during precipitation are not known since H_2SO_4 is produced during iron hydrolysis and during the precipitation of alkali jarosite compounds. In another set of experiments in the same study, a pH_i value of 1.6 was used for each test and the Na_2SO_4 concentration was varied from 0.005M to 0.20M. Both the precipitate yield and the Na concentration of the natrojarosite decreased sharply when less than the stoichiometric amount of Na was present. The decrease in the Na content of the precipitate was presumably due to H_3O^+ substitution. At the lowest alkali concentrations, Na-bearing hydronium jarosite formed.

In other work, dilute aqueous acid solutions containing dissolved Na_2SO_4, K_2SO_4, and $Fe_2(SO_4)_3$ were heated in flasks in an oil bath at temperatures of 114 and 150°C for 72 hours (6). The alkali:sulfate ratio in the precipitate was closer to the theoretical stoichiometry at 150°C, implying that the degree of H_3O^+ substitution was less at the higher temperature and pressure.

In another study, the degree of H_3O^+ substitution increased from 36% (atomic) to 50% when the reaction temperature increased from 50°C to 90°C, respectively (31). The authors believed that the degree of H_3O^+

substitution probably increased with temperature because the rate of crystallization of hydronium jarosite approached that of natrojarosite at the higher temperatures (31). Thus, increasing the temperature appeared to have a larger affect on the kinetics of forming hydronium jarosite than on the kinetics of forming natrojarosite. It was reported that H_3O^+ substitution is more extensive in natrojarosite than in jarosite for a given set of reaction conditions.

Hydronium ion substitution for the alkali metal was also studied for jarosite compounds prepared by heating acidic solutions of ferric and alkali sulfates for 1.5 to 3 hours at 95°C. In that study, Na and K jarosites had apparent H_3O^+ substitutions of 18 and 14 mole percent, respectively (4).

Other researchers were unable to synthesize jarosite or natrojarosite having theoretical compositions using reaction times of four hours and reaction temperatures of 95-210°C, even when a 4-fold excess of alkali was present (22). Instead, hydronium alkali jarosites with excess water and deficient in Fe were formed. For those tests, $Fe_2(SO_4)_3$ and either alkali sulfates or hydroxides were used. The author reports that a high H_3O^+ content in the precipitate was always obtained at about 95°C, and diluting the starting solutions led to increased H_3O^+ substitution. A maximum of 67 to 75% of the theoretical alkali and only 83 to 98% of the theoretical Fe was obtained for the alkali jarosite compounds.

In another study, hydronium/potassium jarosites were synthesized at ambient pressure from aqueous solutions at 85°C for 13 to 3600 hours (30). Results of XRD, IR, and TGA analyses suggested that hydronium jarosite is not a stable phase in K-bearing solutions. Precipitates collected after only 13-24 hours were enriched in H_3O^+, but over time were found to react with the K in solution to form K-rich jarosite (30). An equilibrium composition was not reached in 3600 hours.

Finally, in a study in which jarosite was precipitated from natural thermal water at room conditions over a period of about 13 years, no hydronium ion was detected in the jarosite by IR spectroscopy (27). This was based on the absence of the IR absorption band characteristic of H_3O^+ at 1730-1750 cm^{-1}. Detection limits were not discussed. In another study in which jarosite compounds were formed at room temperature, the jarosite compounds appeared to have close to the theoretical composition based on analyses by XRD, TGA, and DTA (28). The presence of H_3O^+ in hydronium jarosite was established by the IR absorption band in the 1740 cm^{-1} region, while no hydronium ion was detected in the other jarosite compounds.

Based on the literature pertaining to H_3O^+ substitution in jarosite compounds, the conditions which minimize the degree of substitution are not well defined. Limited information is available on the degree of substitution as a function of various reaction parameters, including pH, temperature, and reaction time. Based on results of IR spectroscopy, some researchers report that jarosite compounds having close to theoretical compositions were prepared after a period of months to years at room temperature, although detection limits for the determinations by IR were not discussed (27,28). Because some researchers have reported that jarosite synthesized at 85°C contained less H_3O^+ as the reaction time increased from hours to weeks, the apparent low degree of H_3O^+

substitution in jarosite compounds may be partially attributable to the long reaction times necessary.

Although information on the degree of H_3O^+ substitution as a function of temperature is minimal, it appears that the degree of substitution increases with temperature up to 100°C, but then decreases with further increases in temperature in the range of 110-150°C. The decrease in the degree of substitution with increasing temperature above 100°C may be related to pressure effects at those temperatures.

Kinetics/Thermodynamics

The kinetics involved in the precipitation of jarosite compounds are complex, and determining kinetic parameters has been complicated by the fact that the Fe concentration and pH both change during the reaction (19). Thus, little information is available on reaction rates. However, some maximum reaction rates are given based on the results of one study. These are shown in Table 3. In that study, NaOH was used as the source for the alkali metal.

Although the reactions associated with precipitating jarosite compounds have two major phases with initial reaction periods necessary for formation of Fe species, the reactions are complete after 4-6 hours at 95°C (19). The rate of crystallization decreases from K to Na to H_3O jarosite in the temperature range of 50-90°C (31). Jarosite is also preferred to natrojarosite thermodynamically, as shown below (19):

$$\text{natrojarosite} + K^+ \longrightarrow \text{jarosite} + Na^+ \qquad \Delta G^o = -5.3 \text{ kcal/mole}$$

Table 3. Maximum rate of Fe^{3+} precipitation (v_{max}, g liter^{-1} min^{-1}) at different temperatures[a]

	$10^3 v_{max}$		
m[b]	50°C	70°C	90°C
1	not given	not given	0.05
2	0.01	0.16	0.79
3	0.58	0.71	1.31
4	3.20	2.90	3.33
5	5.00	6.67	6.63
6	8.57	8.74	10.0

[a] Cited from reference 31.

[b] Molar ratio of NaOH:$Fe_2(SO_4)_3$.

For jarosite compounds formed at 115 and 150°C, there is a preference for K over Na in the crystal structure, which is more pronounced at the lower temperature (6). The stability of hydronium jarosite increases with increased temperature in the range of 50-90°C (19).

Brown calculated the standard free energy of formation (ΔG^o_{298}) of jarosite synthesized under room conditions using a mixture of iron and alkali sulfates (23). A value of -783 ± 20 kcal/mole was calculated from its formation and a value of -763 ± 6 kcal/mole was calculated based on its dissolution to equilibrium.

In one study, jarosite was formed in a sample of natural thermal water under room conditions after about 13 years (27). The jarosite was found to have a composition of $(K_{0.9}Na_{0.1})Fe_3(SO_4)_2(OH)_6$ and a standard free energy of formation of -789.3 ± 0.8 kcal/mole. This value and standard thermodynamic constants were used to calculate a value of -790.1 ± 1.0 kcal/mole for pure jarosite. The authors state that published values of ΔG^o_{298} for jarosite are not consistent with their work. They felt that Brown's value of -763 kcal/mole for synthetic jarosite was in error due to arithmetical and analytical errors. However, when the authors recalculated Brown's values using some of their own data, the values were in better agreement (27).

In another study, the ΔG^o_{298} values for jarosite compounds were obtained by analyzing solutions in equilibrium with precipitates synthesized with iron and alkali sulfates at 25 ± 5°C for 15 months (28). The ΔG^o_{298} values obtained in that study are shown in Table 4 below.

Table 4. ΔG^{o}_{298} values for jarosite compounds formed at 25°C[a]

Jarosite Compound	$\Delta G^{o}298$ Value (kcal/mole)
Jarosite	-788.6 ± 1.0
Natrojarosite	-778.4 ± 2.0
Hydronium jarosite	-772.5 ± 2.0

[a] From reference 28.

Summary

Under certain conditions, precipitation of jarosite compounds can be used to remove Fe, Na, and SO_4^{2-} impurities from chemical process streams. Precipitation of these compounds is desirable in view of the fact that they settle rapidly, are easily filtered and dried, and have low solubilities in water. Information on precipitating jarosite compounds comes primarily from patents and from literature on the Jarosite Process and laboratory studies. The information in the literature contains numerous reporting ambiquities and a wide diversity of experimental procedures and reaction conditions. The reaction pathways for precipitating jarosite compounds and the kinetics of the reactions are not well understood.

Conclusions

The precipitation of jarosite compounds is sensitive to numerous reaction variables, including pH, temperature, ion concentrations, and iron:alkali mole ratios. Temperature and pH appear to be particularly important. A pH value of less than 2 and reaction temperatures of about 95°C are necessary to precipitate alkali jarosite compounds most effectively when operating at atmospheric pressure.

Although alkali jarosite compounds have been synthesized under a wide range of temperatures, ion concentrations, and Fe:alkali metal mole ratios, various ambiguities in reporting pose problems in identifying optimum reaction conditions. The lack of clarification regarding the pH in many of the studies is of particular importance.

Additional work is needed to more fully define the optimum reaction conditions and solution compositions that will minimize the incorporation of hydronium ions into the crystal structure of jarosite compounds. In applications where jarosite compounds are being precipitated to remove alkali metals, the hydronium ion substitution for the alkali metal diminishes the effectiveness of the process and increases costs. More research is also required to clarify the mechanisms by which divalent ions substitute for the iron, and whether some of the divalent ions even substitute at all. In addition, the stability of jarosite compounds under various disposal conditions should be evaluated more fully, particularly with respect to the leachability of toxic metals which may be incorporated in these compounds.

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SECTION I.

PRECIPITATION OF IRON, SODIUM, AND POTASSIUM IMPURITIES FROM SYNTHETIC SOLUTIONS MODELING SPENT ACID STREAMS FROM A CHEMICAL COAL CLEANING PROCESS

PRECIPITATION OF IRON, SODIUM, AND POTASSIUM IMPURITIES FROM SYNTHETIC SOLUTIONS MODELING SPENT ACID STREAMS FROM A CHEMICAL COAL CLEANING PROCESS

by

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ABSTRACT

Experiments on treating model spent acid streams from a chemical coal cleaning process by double salt precipitation indicated that simple heating of solutions containing $Fe_2(SO_4)_3$, Na_2SO_4, and K_2SO_4 caused jarosite ($KFe_3(SO_4)_2(OH)_6$) to form preferentially to natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), and precipitate yields were higher than when Na_2SO_4 was the only alkali sulfate present. Virtually all of the K, about 90% of the Fe, and about 30% of the SO_4^{2-} could be precipitated at 95°C, while little or no Na was removed. However, simply heating $Fe_2(SO_4)_3/Na_2SO_4$ solutions up to 95°C for ≤ 12 hours did not produce adequate precipitate yields. When Na was the only alkali metal present, the Fe concentration in the solution had to be increased to avoid formation of undesirable iron compounds. Increasing the Fe concentration to about 6 g/L by adding excess $Fe_2(SO_4)_3$ suppressed the formation of undesirable iron salts and increased natrojarosite yields significantly, but the amount of precipitate obtained was less than half of the theoretical yield based on concentrations of the ions in solution. When either $CaCO_3$, $Ca(OH)_2$, or ZnO was used to maintain a pH value of 1.5 in solutions of $Na_2SO_4/Fe_2(SO_4)_3$ containing excess Fe, precipitate yields increased dramatically at 80 and 95°C. When $CaCO_3$ was used, the precipitate consisted of natrojarosite and gypsum ($CaSO_4 \cdot 2H_2O$). In one of the tests, at least 99% of the Fe and 50-75% of the Na was removed. Complete removal of Na in those tests was probably precluded by hydronium ion substitution for the Na.

INTRODUCTION

It has been estimated that the petroleum resources in the U.S. constitute less than 10% of the total U.S. fossil fuel reserves, but account for over 40% of the domestic energy consumption (1). Coal resources in the U.S. are relatively large compared to petroleum resources, and domestic coal reserves have been estimated to be nearly 300 billion tons (2). Unfortunately, much of this coal contains high levels of sulfur and ash which should be removed by chemical or physical methods prior to combustion. It may be possible to alleviate the problem of our rapidly depleting oil resources by producing an ultraclean coal product which can be pulverized and mixed with water to form coal-water slurries. These slurries could then be burned subsequently as an alternate fuel to replace oil.

The TRW Gravimelt Process, also known as the Molten Caustic Leaching (MCL) Process, is one experimental chemical coal cleaning technique which produces a low-ash, low-sulfur coal product that could be suitable for producing coal-water slurries. In this process, coal is treated with molten NaOH or NaOH/KOH mixtures at 300-400°C for 1-3 hours (3-9). After washing the caustic-treated coal with water, it is washed with dilute H_2SO_4 to remove Fe, ionically bound alkali, and other acid-soluble salts remaining on the caustic-leached and water-washed coal. A typical flow diagram for the MCL Process is shown in Figure 1. During this cleaning process, a spent acid solution containing significant amounts of Na, K, Fe, and SO_4^{2-} salts is produced. This acid stream requires cleaning before it can be discharged to the environment or recycled back into the leaching process. One of the proposed treatment

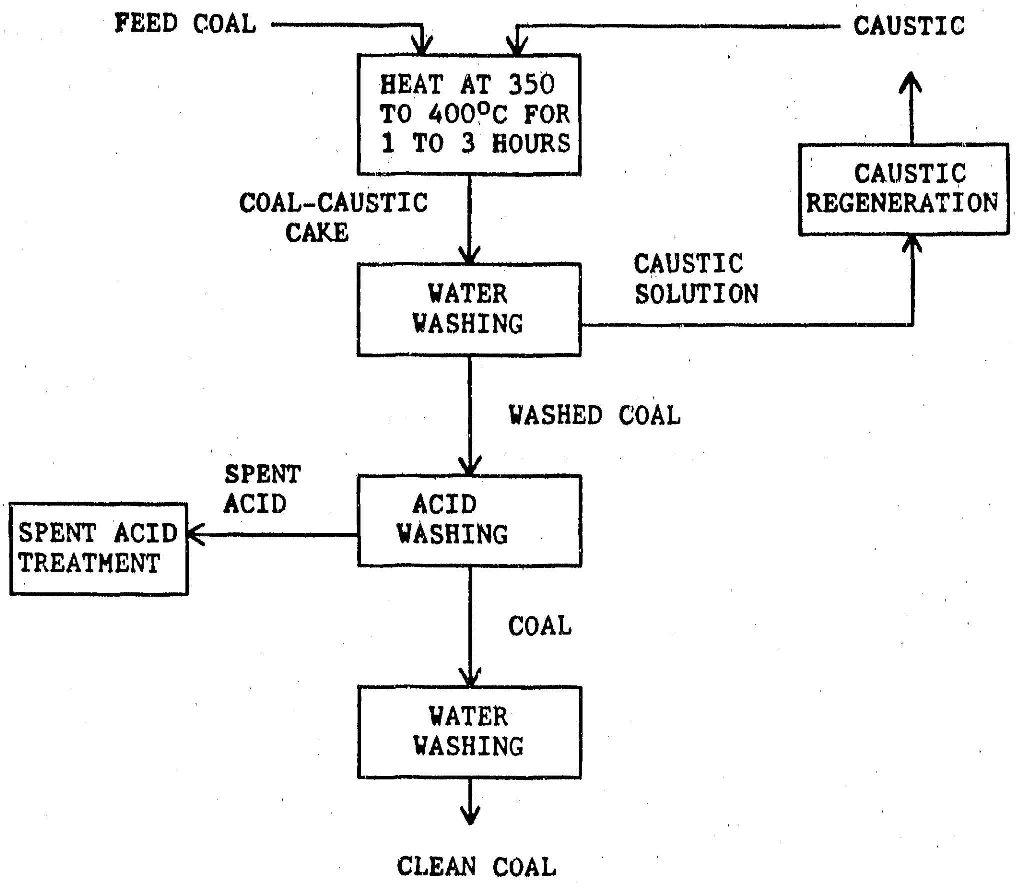

Figure 1. General schematic flow diagram for the TRW MCL process

methods for the acid wash solution is to precipitate the Fe, Na, and SO_4^{2-} impurities as jarosite compounds, i.e., double salts of Na (or K) and Fe.

It has been predicted that the spent acid would have alkali sulfate concentrations of 2.5 - 5 g/L and ferric sulfate concentrations of 5-10 g/L (6). This corresponds to 0.8-1.6 g/L of Na, 1.4-2.8 g/L of Fe, and 5.3-10.6 g/L of SO_4^{2-}. Thus, the anticipated Fe:Na mole ratios are between 0.4 and 1.4.

In this work, laboratory experiments were performed on model solutions simulating the spent acid stream to determine whether the Na, K, Fe, and SO_4^{2-} could be precipitated as jarosite ($KFe_3(SO_4)_2(OH)_6$) and natrojarosite ($NaFe_3(SO_4)_2(OH)_6$). Reaction times up to 12 hours and temperatures of 80^oC, preferred by TRW (10), were used as a guide in the experiments with the model solutions. Jarosite-type double salts are generally crystalline and can be easily dewatered and dried. In addition, they have low solubilities in water and therefore may not pose a waste disposal problem (11). An emphasis was placed on studying the precipitation of natrojarosite, although some precipitation of the potassium jarosite species was also performed. These results are from exploratory research intended to investigate the feasibility and practicality of this approach to treatment of the spent acid stream from the chemical coal cleaning process. Thus, the primary purpose of these experiments was to study the removal of Na, Fe, K, and SO_4^{2-} as jarosite-type double salts as a function of various reaction parameters. In addition, the yield and mineralogical composition of the precipitates provided valuable information needed to assess more fully the effectiveness of this treatment approach. In some of the experiments, only the precipitate yield and composition were used as indirect indicators of the degree of purification of the solutions.

BACKGROUND

In the Jarosite Process used in hydrometallurgical processing of zinc, the leach solutions are typically heated to about 95°C while maintaining a pH of 1.5 by adding roasted ZnS ore to neutralize acid liberated during the reactions (12-14). Under these conditions, the precipitation of jarosite compounds is typically completed within about 6 hours (15). Good agitation is desirable to ensure rapid mixing of the reactants, promote crystal growth, and to keep the precipitate in suspension (12). The rate of iron precipitation as alkali jarosite compounds increases with increasing temperature, alkali ion concentration, and pH (12). The rate of the Fe precipitation also increases as the Fe concentration increases, but the rate appears to be independent of the alkali concentration once the stoichiometric amount of alkali metal is present (12,15). Some patents on jarosite precipitation from industrial waste streams indicate that the Fe^{3+} concentration should be about 4 g/L or more (11). The effect of seeding to enhance the precipitation of jarosite compounds is not clear, and it is not certain whether seeding is even needed (15).

Jarosite compounds have been synthesized in the laboratory under a wide variety of conditions. These include temperatures of 25 to 200°C, reaction times of hours to months, ion concentrations of 1 to 50 g/L, initial pH values of 1 to 3, and Fe:Na/K mole ratios of 0.2 to more than 10 (16-18). In many cases, the pH of the solution was initially adjusted to a specific value prior to heating, with no subsequent pH adjustments, and the pH of the solution was allowed to change during the precipitation of the jarosite compounds. According to one patent, the preferred pH range for precipitating natrojarosite is 1.8 to 2.5, although it is not clear whether these are initial pH values or whether the pH is maintained during the reactions by using a neutralizing agent (11).

Hydronium ion (H_3O^+) substitutes for a portion of the alkali metal in jarosite compounds (17-19). Thus, although the theoretical composition of jarosite compounds is $MFe_3(SO_4)_2(OH)_6$, where M could be an alkali metal such as Na or K, the actual composition for most natural and synthetic jarosite compounds is $M_{(1-x)}(H_3O)_xFe_3(SO_4)_2(OH)_6$, where "x" is typically 0.15 to 0.25 (19).

The reactions for precipitating jarosite compounds require an initial period to form the necessary iron species, but the reactions are complete after about 6 hours at 95°C (15). In the temperature range of 50-90°C, the rate of crystallization decreases from the K to Na to hydronium jarosites (20). Jarosite is favored both thermodynamically (15,16) and kinetically (20) over natrojarosite.

EXPERIMENTAL METHODS

Reagents

Reagent-grade H_2SO_4, Na_2SO_4, and $Fe_2(SO_4)_3 \cdot xH_2O$ (ferric sulfate) were used for all of the experiments. One of the variables affecting the determination of the theoretical concentration of ferric iron in the starting solution was the water content of the $Fe_2(SO_4)_3 \cdot xH_2O$. For consistency, the $Fe_2(SO_4)_3 \cdot xH_2O$ was dried prior to use. However, when the ferric sulfate was dried for several hours at 110°C, analyses for Fe indicated that the material was not anhydrous. Portions of the original (undried) material were subsequently dried for about 24 hours at 180°C, chosen on the basis of temperature limitations of the oven. X-ray diffraction (XRD) analysis of this dried material suggested that it was largely anhydrous. In addition, two different analysts used spectrophotometry to obtain 25.8% and 26.4% Fe in the dried $Fe_2(SO_4)_3$. Theoretical Fe concentrations are 25.6% for the dihydrate and 26.7% for the monohydrate. Thus, the chemical and XRD analyses indicated that the dried $Fe_2(SO_4)_3$ used in all of the experiments contained between 0 and 2 water molecules per mole. For the purposes of our calculations, the $Fe_2(SO_4)_3$ which was dried at 180°C was always assumed to be the monohydrate form (i.e., 26.7% Fe).

To determine the magnitude of possible errors resulting from the $Fe_2(SO_4)_3$ rehydrating during handling, an aliquot of the dried $Fe_2(SO_4)_3$ was left exposed to laboratory atmosphere on a digital analytical balance for 10 minutes and the weight change was monitored. A continuous increase in weight was observed, but the increase was only about 1% after 10 minutes. Since the dried $Fe_2(SO_4)_3$ used for precipitation experiments was never exposed to the air for more than 5 minutes, errors associated with incorporation of moisture during handling should not be significant.

The Na_2SO_4 was dried at 110°C for about 24 hours prior to use, although virtually no weight loss was observed. All solid chemicals were stored in a desiccator when not in use.

General Experimental Procedure

A schematic diagram of the experimental procedure is shown in Figure 2. All tests were performed using beakers on hot plate/stirrers. The beakers were covered to minimize evaporative losses and the solutions were stirred continuously at a moderate rate to provide good mixing. The pH was measured with a pH meter (Altex Model 2000 Ion Analyzer) using the temperature-compensation dial for measurements at higher temperatures. The water was first acidified to the desired pH with H_2SO_4, then heated to 40-50°C, and the $Fe_2(SO_4)_3$ was added. The temperature was maintained for about 15 minutes, the Na_2SO_4 was added, and the solution was heated to the desired temperature.

After the completion of each test, the solutions were allowed to cool for about 5 minutes. The precipitates were filtered from the hot solutions using Gelman GN-6 0.45-micron membrane filters in a Gelman Magnetic Filter Funnel with an Erlenmeyer flask and a water aspirator. When the amount of precipitate was small (e.g., <0.2 g), most of the precipitate was coating the walls of the beaker and had to be scraped off. In such cases, losses probably were affecting the total

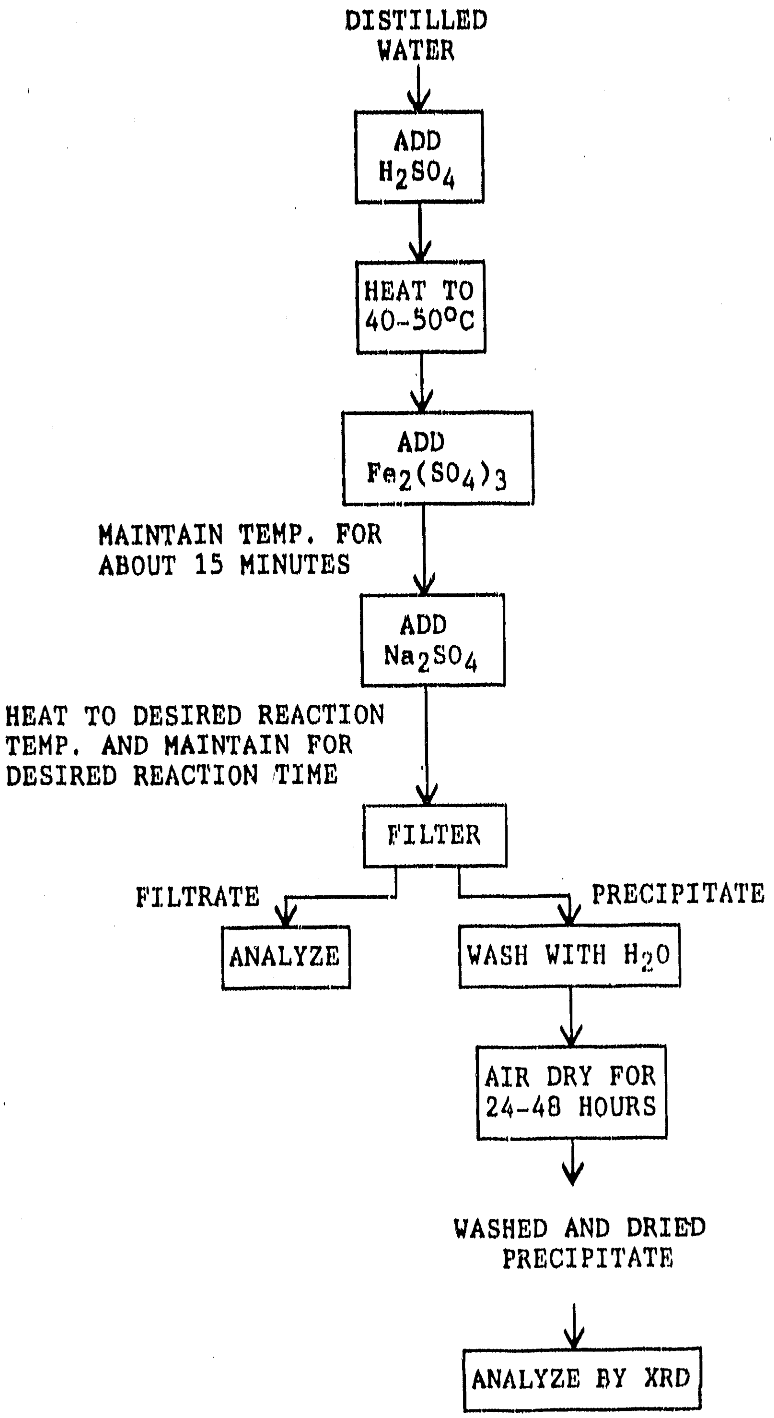

Figure 2. Experimental procedure used in this study

precipitate yield. After collecting an aliquot of the filtrate for subsequent analyses, the precipitates were rinsed extensively with small portions of distilled water and then air-dried for 1-2 days. Air drying was preferred to oven drying to minimize alteration of the sample that could interfere with possible thermal analysis studies on these samples planned in the future. To test the adequacy of this drying procedure, four air-dried precipitates from different tests were dried in an oven at 110°C for 2 hours. The weight loss was less than 0.2%, indicating that any variability in the moisture contents of the air-dried precipitates should be negligible.

Several sets of experiments were performed using acidic $Fe_2(SO_4)_3$ solutions containing either Na_2SO_4, K_2SO_4, or their mixtures. Reaction times of six hours were selected for most of the tests. Some of the tests were run at 95°C since the Jarosite Process operates typically at that temperature. The experiments performed in this study are summarized in Table 1. Each set of experiments is discussed separately in more detail below.

Experiments with $Na_2SO_4/Fe_2(SO_4)_3$ Solutions (Heating Only)

Because jarosite compounds are often synthesized without any pH adjustments, initial experiments were performed to ascertain whether they could be effectively precipitated by simply heating solutions containing predicted concentrations of Na, Fe, and SO_4^{2-}. For these tests, 1.25 g Na_2SO_4 and 3.70 g $Fe_2(SO_4)_3$ were added to 500 mL of water acidified with H_2SO_4. The $Fe_2(SO_4)_3$ level was chosen so that the Fe:Na

Table 1. Summary of experimental conditions used in this study

Experimental[a,b] Variable(s)	mL	$Fe_2(SO_4)_3$ (g)	$Fe_2(SO_4)_3$ (g/L)	[Fe] (g/L)	M_2SO_4[c] (g)	M_2SO_4[c] (g/L)	pH_i Value	Reaction Temp. (°C)	Reaction Time (hrs)
pH_i, Temp. (Table 2)	500	3.70	7.4	2	1.25	2.5	1.5–2.7	60–95	6
pH_i (Table 3)	500	11.0	22.2	6	1.25	2.5	1.8–2.7	95	6
Time (Fig. 4)	250	5.55	22.2	6	0.63	2.5	1.8, 4.0	80, 95	1, 3, 6, 9
Seeding (Table 4)	250	5.55	22.2	6	0.63	2.5	1.8, 4.0	80, 95	6
Adding K_2SO_4 (Table 5)	250	5.55	22.2	6	0.63[d]	2.5[d]	1.8, 4.0	80, 95	6
Acid Neutral. (Table 6)	250	14.0	56	15	1.25	5.0	4.0	80, 95	6

[a] pH_i is the starting pH of the solution.

[b] For a given set of experimental conditions, the corresponding figure or table is given in parentheses.

[c] Na_2SO_4 unless otherwise noted.

[d] Used either Na_2SO_4, K_2SO_4, or 1:1 (wt.) mixtures of the two alkali sulfates.

mole ratio was about 1:1, which resulted in a concentration of about 2 g Fe/L. The solutions were heated for 6 hours at 60, 70, 80, and 95°C and pH_i values of 1.5, 1.8, 2.1, 2.4, and 2.7.

Because some patents on jarosite precipitation from industrial waste streams indicate that the Fe^{3+} concentration should be about 4 g/L or more (11), additional tests were performed at 95°C in which the Fe^{3+} concentration was tripled to about 6 g/L, resulting in Fe:Na mole ratios of 3:1.

Precipitate yield as a function of reaction time was studied at 80 and 95°C and pH_i values of 1.8 and 4.0 using reaction times of 1, 3, 6, and 12 hours. As with the previous experiments, the Fe concentrations were about 6 g/L. These tests were performed using volumes of 250 mL rather than 500 mL, and the reagent amounts were scaled back accordingly. Several of these tests were repeated with natrojarosite seeding to determine if yields could be improved.

Experiments with $Na_2SO_4/K_2SO_4/Fe_2(SO_4)_3$ Solutions
(Heating Only)

In another set of experiments, solutions of $Fe_2(SO_4)_3$ with Na_2SO_4, K_2SO_4, or 1:1 (weight) mixtures of Na_2SO_4 plus K_2SO_4 were used to form potassium and sodium jarosite. In each of these tests, elevated $Fe_2(SO_4)_3$ levels were selected to produce a concentration of 6 g Fe/L. Thus, for these tests, 0.63 g alkali sulfate and 5.55 g $Fe_2(SO_4)_3$ were added to 250 mL of water, and the solutions were heated for six hours at 80 or 95°C at pH_i 1.8 or 4.0.

Experiments Using Acid Neutralization in $Na_2SO_4/Fe_2(SO_4)_3$ Systems

In other work, tests were performed with model solutions using the maximum predicted concentration of Na_2SO_4 (i.e., 5 g/L) and Fe concentrations which were 25% in excess of a 3:1 Fe:Na mole ratio (i.e., the Fe:Na mole ratio in natrojarosite). Because some of the Fe precipitates as hydronium jarosite, the excess Fe helped ensure that sufficient iron was available to precipitate all the Na as natrojarosite. No K_2SO_4 was present in these tests. Solutions were prepared by adding 14.0 g $Fe_2(SO_4)_3$ and 1.25 g Na_2SO_4 to 250 mL of water acidified with H_2SO_4 to an initial pH of 4.0. The solutions were stirred and heated for six hours at either 80°C or 95°C. These tests were performed with and without the addition of a neutralizing agent to maintain a pH value of 1.5. The neutralizing agents used were ZnO, $Ca(OH)_2$, or $CaCO_3$.

Analytical Procedures

Iron was determined spectrophotometrically using 1,10-phenanthroline, and Na and K were determined by ion chromatography (IC) using standard procedures. In some tests, sulfate concentrations in the final solutions were determined using IC. Total sulfur was determined on one of the precipitates by using a high-temperature combustion method to determine whether one of the inorganic phases being precipitated contained significant amounts of sulfur.

The precipitates were analyzed by x-ray diffraction (XRD) using a Picker theta-theta x-ray diffractometer utilizing Mo K-alpha radiation.

The samples did not require grinding prior to XRD analyses. Data were collected while scanning from 3.0 to 30° two-theta in increments of 0.05° two-theta with a counting time of 1 second per step. The XRD patterns obtained were computer-generated plots of two-theta values versus relative peak intensity. In addition, a software package provided a listing of peak positions and distances between atomic planes in the crystal lattices ("d" values) by using the Bragg equation (21) to convert the experimental peak positions to "d" values. Compounds were identified by comparing these "d" values to those in standard JCPDS files (22) and by comparing the diffraction patterns with those obtained previously at this laboratory on pure samples of the individual mineralogical components.

RESULTS

Experiments with $Na_2SO_4/Fe_2(SO_4)_3$ Solutions
(Heating Only)

Several sets of experiments were performed by heating solutions of Na_2SO_4 and $Fe_2(SO_4)_3$ without addition of any other chemicals. These studies are each described (individually) below.

Effect of reaction temperature and initial pH

Experimental conditions and results of chemical and mineralogical analyses for tests with Fe concentrations about 2 g/L are shown in Table 2. The pH at the start of precipitation was typically in the range of 1.4-1.8, regardless of pH_i prior to the addition of any chemicals. The pH of the final solution was slightly higher at lower temperatures, but it was fairly consistent over the pH_i range of 1.5-2.7 at a given temperature. Based on the XRD results, natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) appeared to be the only double salt formed. In some of the tests, contaminant compounds also precipitated. The contaminants were largely amorphous and did not produce well-defined XRD peaks. However, the major components appeared to consist largely of iron hydroxides. Analysis for total sulfur of a contaminant mixture indicated about 2.5 wt. % S. Thus, the contaminants do not appear to be composed of significant amounts of sulfate. Typical XRD patterns for the natrojarosite and for the contaminants are shown in Figure 3.

As can be seen from the data in Table 2, the quantity of precipitate increased with increasing the pH_i from 1.5 to 2.7 and

Table 2. Precipitation yields using predicted concentrations of Na_2SO_4 and $Fe_2(SO_4)_3$[a,b]

Temp. (°C)	pH Init.	pH final	Yield (g)	% Fe Removed	% Na Removed	Compounds[c] Natro-jarosite	Compounds[c] Other[d]
95	2.7	1.4	1.42	80	15	n.d.	XXX
95	2.4	1.4	1.38	78	12	n.d.	XXX
95	2.1	1.4	1.21	68	17	X	XXX
95	1.8	1.4	1.18	58	22	XX	XX
95	1.5	1.5	0.24	8	20	XXX	n.d.
80	2.7	1.6	0.98	49	10	X	XXX
80	2.4	1.7	0.82	38	12	X	XXX
80	2.1	1.6	0.89	41	20	XXX	X
80	1.8	1.7	0.16	15	20	XXX	n.d.
80	1.5	1.5	0.00	7	10	---	---
70	2.7	1.9	0.39	54	15	XX	XX
70	2.4	1.9	0.39	55	12	XXX	X
70	2.1	1.9	0.08	8	7	XXX	n.d.
70	1.8	1.8	0.01	13	15	XXX	n.d.
60	2.7	2.1	0.01	10	10	XX	XX
60	2.4	2.1	0.01	1	5	XXX	n.d.
60	2.1	2.0	0.00	4	5	---	---
60	1.8	1.8	0.00	3	12	---	---

[a] See Appendix III for all experimental data.

[b] 500 mL solution containing 1.25 g Na_2SO_4 and 3.70 g $Fe_2(SO_4)_3$ (i.e., 0.99 g Fe, 0.41 g Na and about 3.4 g SO_4^{2-}) heated for 6 hours.

[c] Relative amounts based on x-ray diffraction: X=small; XX=medium; XXX=large; n.d. = not detected.

[d] Miscellaneous iron compounds such as iron hydroxides.

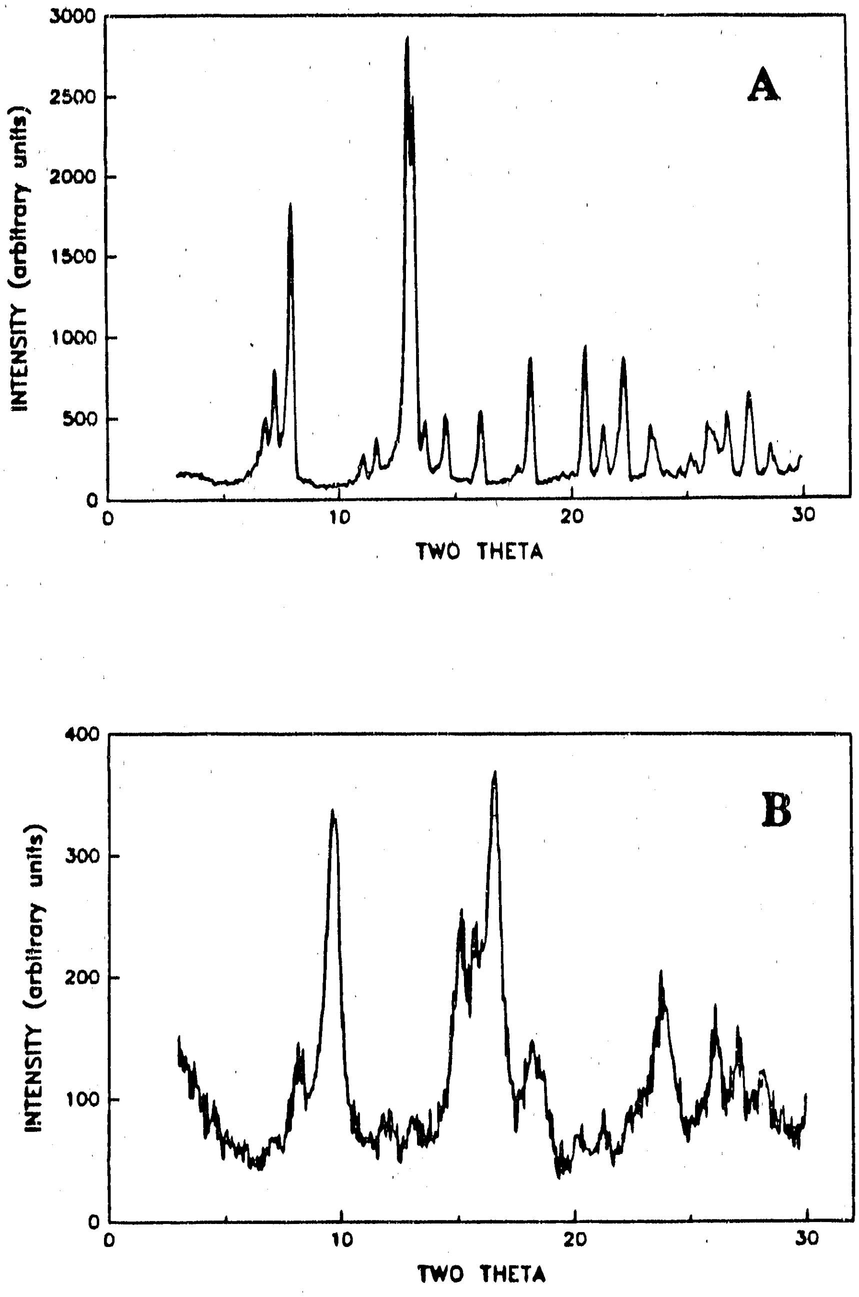

Figure 3. Typical XRD pattern for natrojarosite (A) and contaminant phases (B)

increasing the temperature from 60 to 95°C. However, as shown by the relative amounts of natrojarosite and contaminants obtained by XRD, the increased yields were due predominantly to increased levels of contaminant phases rather than to increased amounts of natrojarosite. The relative concentrations of impurities decreased with decreasing pH_i and temperature.

Analyses of the filtered solutions indicated that substantial amounts of Fe were removed, although this was predominantly a result of the precipitation of contaminant phases. Thus, significant Fe removal occurred with minimal formation of natrojarosite. The percent Fe removed from the solutions correlated well with precipitate yields, except where minimal precipitate was formed. The Na concentrations in the filtrates did not vary with either temperature or pH. The Na concentrations measured in the filtrates were lower than the initial concentrations, even in the absence of precipitate formation. When natrojarosite alone was produced, the precipitate yields were generally less that 10% of the theoretical maximum natrojarosite yield based on concentrations of Na, Fe, and SO_4^{2-} in the starting solutions.

Effect of tripling the $Fe_2(SO_4)_3$ concentration

Results of the experiments at 95°C with solutions of Na_2SO_4 and excess $Fe_2(SO_4)_3$, at about 6 g Fe/L, are shown in Table 3. The final pH values for these tests ranged from 1.2 to 1.4. Some of the tests shown in Table 3 were taken from Table 2 and are included here for comparative purposes. In test 1 (taken from Table 2), predicted concentrations of the sulfate compounds were used at a pH_i value of 1.8. When the Fe

Table 3. Effect of pH and elevated levels of $Fe_2(SO_4)_3$ on precipitate yield and composition from Na_2SO_4 solutions[a,b]

			Iron		Sodium		Compounds[c]	
Test No.	Initial pH	Ppt. Wt. (g)	Initial Grams	% Removed	Initial Grams	% Removed	Natro-jarosite	Other[d]
1	1.8	1.18	0.99	58	0.41	22	XX	XX
2	1.8	2.11	2.97	28	0.41	29	XXX	n.d.
3	1.8	5.11	2.97	64	1.23	22	XXX	n.d.
4	2.4	1.38	0.99	78	0.41	12	n.d.	XXX
5	2.4	3.32	2.97	42	0.41	24	XXX	n.d.
6	2.7	1.42	0.99	80	0.41	15	n.d.	XXX
7	2.7	4.10	2.97	49	0.41	29	XXX	n.d.

[a] See Appendix III for all experimental data.

[b] 500 mL solution containing either 1.25 or 3.75 g of Na_2SO_4 and either 3.70 or 11.1 g of $Fe_2(SO_4)_3$ heated for 6 hours at 95°C.

[c] Relative amounts based on x-ray diffraction: X=small; XX=medium; XXX=large; n.d. = not detected.

[d] Miscellaneous iron compounds such as iron hydroxides.

level was tripled by adding $Fe_2(SO_4)_3$ (test 2), the yield increased by a factor of two and the precipitate contained natrojarosite alone rather than a mixture of natrojarosite and contaminants. Thus, increasing the Fe concentration appeared to suppress the formation of the contaminant phases. However, since the Fe:Na mole ratio of 3:1 was coincidentally the same as that of natrojarosite in that test, it is not clear if suppression of the contaminant phases was due to the increased Fe levels or the fact that the Fe and Na concentrations in the solution now matched the theoretical stoichiometry of natrojarosite. To elucidate the effect of reaction stoichiometry, test 3 was conducted in which both Fe and Na were tripled by adding the respective sulfate salts to the solution. Thus, the Fe:Na mole ratio in the solution was 1:1 as in the previous tests for which the Fe concentration was about 2 g/L. Since contaminant phases were not detected by XRD in the precipitate from test 3, it appears that the suppression of the contaminant phases was due primarily to the increased Fe levels and not the 3:1 Fe:Na mole ratios.

In tests 4 through 7, the effects of tripling the Fe concentration at the higher pH_i values of 2.4 and 2.7 can be seen. As for the lower pH_i value of 1.8, the formation of the contaminant phases was suppressed by increasing the Fe concentration. Based on results shown in Table 2, the critical Fe concentration appears to vary with temperature and pH_i for the concentrations studied.

For the tests in which only the Fe level was tripled (tests 2, 5, and 7), precipitate yield doubled when pH_i was increased from 1.8 to 2.7. At pH_i 2.7, precipitate yields were nearly half of the theoretical amount of natrojarosite that could have formed based on the Na, Fe, and

SO_4^{2-} quantities in solution. Although half of the Fe was removed at pH_i 2.7, only 25% of the Na was removed, possibly due to substitution of hydronium ion for Na in the crystal structure.

Effect of reaction time

Results of the experiments in which precipitate yield was studied as a function of reaction time are depicted in Figure 4. For these tests, the theoretical maximum natrojarosite yield was about 4 grams. The precipitate yield increased as the temperature was increased from 80 to 95°C and as pH_i increased from 1.8 to 4.0. At 95°C, the amount of precipitate did not increase substantially after 6 hours. Thus, a critical pH may have suppressed natrojarosite formation under these experimental conditions. At a given pH, yields from reactions for over 3 hours were at least five times higher at 95°C than at 80°C. Thus, under the conditions used, temperature had a much more pronounced effect than pH_i on yield. However, it should be kept in mind that curves depicting yield versus time, temperature, or pH may be significantly different if concentrations of the ions in solution are altered.

Effect of seeding

The effects of seeding with natrojarosite are evident from results presented in Table 4. Precipitate yields increased when seeding was used, particularly at 80°C and a pH_i of 4.0. However, even with seeding, the overall yields were low.

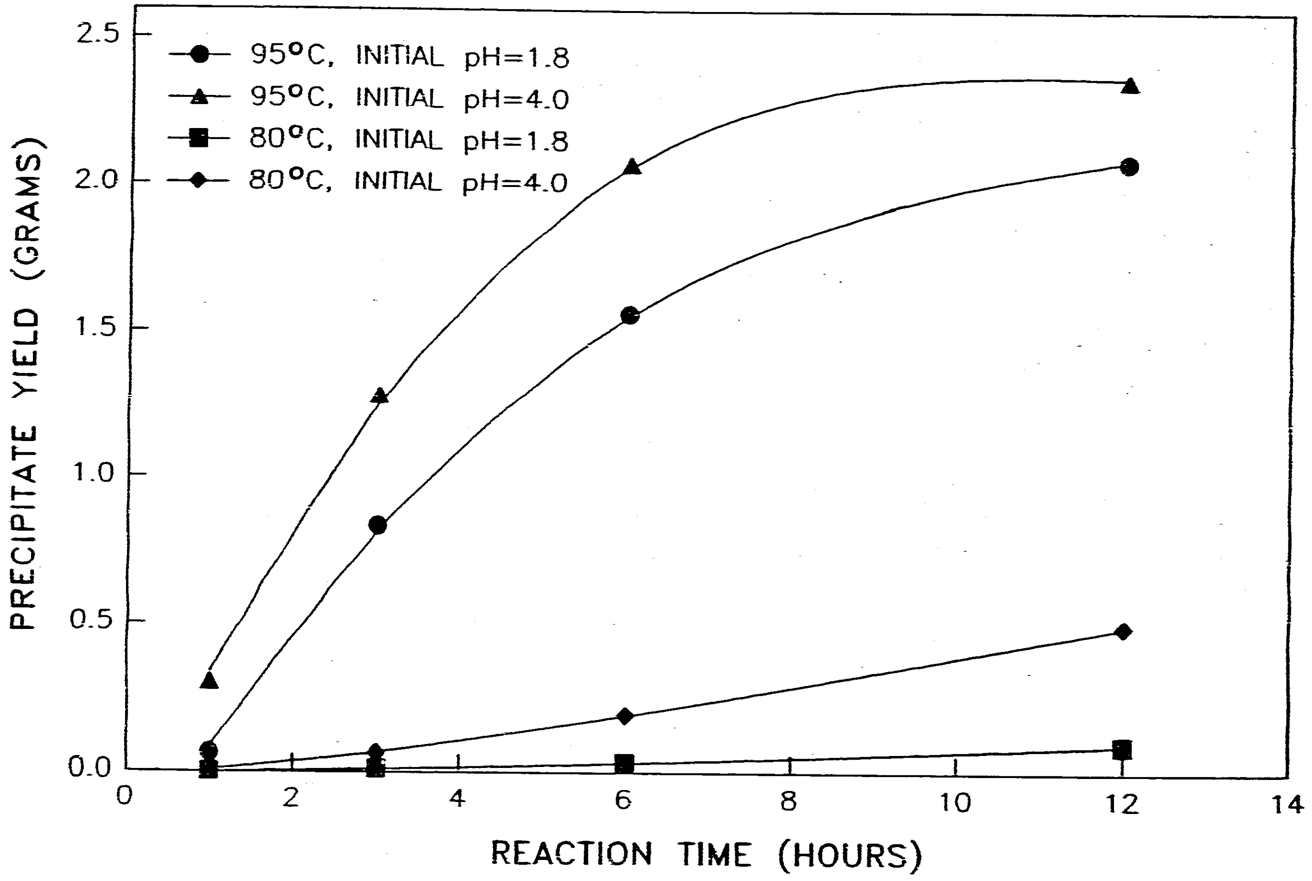

Figure 4. Precipitate yield versus reaction time at reaction temperatures of 80°C and 95°C and initial pH values of 1.8 and 4.0

Table 4. Effect of seeding with natrojarosite on precipitate yield using predicted levels of Na_2SO_4 and elevated levels of $Fe_2(SO_4)_3$[a]

Temp (^oC)	(pH_i)	Weight of Seed (g)	Total ppt. wt. (g)	Ppt. wt. (g) - Seed (g)
95	1.8	0.00	1.57	1.57
95	1.8	0.50	2.80	2.30
95	1.8	1.01	3.20	2.19
80	4.0	0.00	0.19	0.19
80	4.0	0.51	1.71	1.20

[a] 250 mL solution containing 5.55 g $Fe_2(SO_4)_3$ and 0.63 g Na_2SO_4 heated for 6 hours.

Experiments with $Na_2SO_4/K_2SO_4/Fe_2(SO_4)_3$ Solutions
(Heating Only)

Results of the experiments using the mixed alkali sulfate systems are shown in Table 5. In tests 8 through 14, the total concentration of alkali sulfates was at the low end of the concentrations predicted by TRW. For tests 8, 9, 10, and 12, yields at 95°C were increased by 50 to 100% between pH_i of 4.0 and 1.8, respectively, when a mixture of sodium and potassium sulfates was used instead of Na_2SO_4 only. When these tests were repeated at 80°C (tests 11 and 13) rather than 95°C, yields decreased by only 20-25%. Thus, the effect of temperature on yield was much less pronounced with a mixed alkali sulfate system as compared to Na_2SO_4 alone (see results discussed in previous section). When K_2SO_4 was used at pH_i 4.0 (test 14), the yield was twice as high as when Na_2SO_4 was used (test 8) and about 30% higher than the yield obtained with the mixed alkali sulfates (test 10) at the same pH_i value.

In another test, 2.5 g/L of 1:1 (weight) Na_2SO_4 plus K_2SO_4 were added to an acidified solution (pH_i value of 2.7) containing only 2 g Fe/L. When this solution was heated at 95°C for 6 hours, jarosite ($KFe_3(SO_4)_2(OH_6)$) was formed preferentially and no contaminant phases were detected by XRD. In an earlier test (first test shown in Table 2) in which only Na_2SO_4 was used under identical experimental conditions, only contaminant phases were detected. Since contaminant phases did not form with initial concentrations of 2 g Fe/L when both K and Na were present, but formed when only Na was present, the Fe concentration does not appear to be as critical of a factor for suppressing contaminant phases in a mixed Na/K sulfate system as it is in a Na_2SO_4 system.

Table 5. Precipitate yields from solutions of Na_2SO_4 and K_2SO_4 and elevated amounts of $Fe_2(SO_4)_3$[a,b]

Test No.	Temp. (°C)	Initial pH	Ppt. Wt. (g)	% Removed			
				Fe	Na	K	SO_4^{2-}
8	95	4.0	2.07	n.m.[c]	n.m.[c]	---	n.m.[c]
9	95	1.8	1.56	n.m.[b]	n.m.[b]	---	n.m.[c]
10	95	4.0	3.28	74	40	100	36
11	80	4.0	2.47	54	20	>93	24
12	95	1.8	2.97	65	30	100	24
13	80	1.8	2.40	51	10	>93	14
14	95	4.0	4.31	93	---	96	n.m.[c]

[a] See Appendix III for all experimental data.

[b] 250 mL solutions containing 5.55 g $Fe_2(SO_4)_3$ and 0.63 g M_2SO_4 (Na_2SO_4, K_2SO_4, or 1:1 (wt.) Na_2SO_4/K_2SO_4) heated for 6 hours.

[c] n.m. = not measured.

Levels of Fe, Na, K, and SO_4^{2-} in the initial and final solutions are also presented in Table 5. Heating the solutions for 6 hours at either 80°C or 95°C removed almost all of the K, about 90% of the Fe, and about 30% of the SO_4^{2-}, while less than 40% of the Na was removed. The Na removals were low because jarosite formed preferentially to natrojarosite, as suggested by the percent removal of the alkali metals from the solutions. XRD analyses supported the observation that jarosite formed preferentially. The preferential formation of jarosite to natrojarosite is expected based on studies of kinetics and thermodynamics. No contaminant phases or other double salts were detected by XRD in any of these samples.

Experiments Using Acid Neutralization in $Na_2SO_4/Fe_2(SO_4)_3$ Systems

Results of the tests conducted at a constant pH value with a neutralizing agent are shown in Table 6. Maintaining a pH of about 1.5 dramatically increased precipitate yields. At 80°C, about 1% of the solids (by mass) added to the system were precipitated after 6 hours without neutralization. When $CaCO_3$ was added to maintain a pH of about 1.5, more than 80% of the added chemicals (including neutralizing agent) were precipitated. The $CaCO_3$ constituted about 25% of the total weight of the chemicals (i.e., $Fe_2(SO_4)_3$, Na_2SO_4, and $CaCO_3$) added to the solution. It is likely that the yields at 80°C could be increased even further if longer reaction times are used.

Precipitation was more effective at 95°C than at 80°C. When $CaCO_3$ or $Ca(OH)_2$ was used at 95°C, the precipitate weights were essentially

Table 6. Precipitation of the double salt natrojarosite using additives for acid neutralization[a,b]

		Solids Added (g)				
Neutralizing Agent	Temp. (^oC)	$Fe_2(SO_4)_3$ + Na_2SO_4	Neutral. Agent	Total	Precip. Wt. (g)	XRD Analysis
None	80	15.2	0.0	15.2	0.1	Natro.
$CaCO_3$, Test 1	80	15.2	4.5	19.8	14.9	Natro./Gypsum
$CaCO_3$, Test 2	80	15.2	5.0	20.2	16.8	Natro./Gypsum
None	95	15.2	---	15.2	2.8	Natro.
$CaCO_3$, Test 1	95	15.2	6.1	21.4	21.3	Natro./Gypsum
$CaCO_3$, Test 2	95	15.2	n.m.[c]	n.m.[c]	19.3	Natro./Gypsum
$Ca(OH)_2$	95	15.2	4.6	19.8	21.1	Natro./Gypsum
ZnO, Test 1	95	15.2	4.4	19.6	11.4	Natro.
ZnO, Test 2	95	15.2	n.m.[c]	n.m.[c]	10.0	Natro.

[a] 14.0 g $Fe_2(SO_4)_3$ and 1.25g Na_2SO_4 added to 250 mL H_2O and heated for 6 hours.

[b] pH value of 1.5 maintained by acid neutralization.

[c] n.m. = not measured.

equal to the sum of the weights of the reagents in solution. Analyses by XRD indicated that natrojarosite ($NaFe_3(SO_4)_2(OH)_6$) and gypsum ($CaSO_4 \cdot 2H_2O$) were present in the precipitates when $CaCO_3$ was used as a neutralizing agent, while only natrojarosite was detected when ZnO was used. No other compounds were detected in any of the precipitates. When ZnO is used, it reacts with the H_2SO_4 to form H_2O and soluble $ZnSO_4$. Thus, the lower precipitate yields could be attributed to the zinc staying in solution and not co-precipitating with the natrojarosite. Thus, the precipitate yields obtained when using ZnO should not be compared to the total weight of all the chemicals added since some of the reaction products are water-soluble.

XRD analysis of the precipitate and chemical analyses of the filtrate from the second test with $CaCO_3$ at 95°C indicated that at least 99% of the Fe and 50-75% of the Na were removed from the $Na_2SO_4/Fe_2(SO_4)_3$ solution within 6 hours by precipitating natrojarosite. Similar Na removals were observed when using the $Ca(OH)_2$ or ZnO. It is interesting to note that a maximum of 75% of the Na was removed, even though there was 25% more Fe than the stoichiometric amount necessary for complete removal of Na. This is probably due to hydronium ion substitution for the alkali metal in jarosite-type compounds (19).

CONCLUSIONS

Precipitation of double salts in the jarosite family of compounds is complex and sensitive to a number of variables. Based on experiments using predicted concentrations of alkali and ferric sulfate in the spent acid from the chemical cleaning of coal by the MCL Process, the process stream probably cannot be simply heated to precipitate natrojarosite. Although the precipitation of natrojarosite can effectively remove Na, Fe, and SO_4^{2-} impurities from spent acid process streams at 80°C if neutralizing agents are added, Na removal is complicated by hydronium ion substitution for the alkali metal and by the preferential formation of jarosite to natrojarosite. The iron concentration may need to be increased to suppress the formation of contaminant iron compounds, particularly if only NaOH is used for caustic leaching of coal. If the concentration is increased to 5 g Fe/L and the predicted Na concentrations are correct, Fe:Na mole ratios will be between 2.6:1 and 1.3:1. Based on results of this work, natrojarosite is probably the only double salt which will form in appreciable quantities at these mole ratios using the reaction times and temperatures proposed by TRW. However, conditions for precipitating jarosite appear to be less stringent than for precipitating natrojarosite.

In order to precipitate all the Na as natrojarosite, each gram of Na will require at least 7 g of Fe (26 g anhydrous $Fe_2(SO_4)_3$) based on stoichiometry. Similarly, each gram of K will require about 4 g of Fe (about 15 g $Fe_2(SO_4)_3$). Since the amount of Fe originally present in the solution will constitute only about 10-50% (based on the predicted levels of alkali and ferric sulfates) of the theoretical amount required for complete removal of the alkali metal as a jarosite-type compound, significant amounts of $Fe_2(SO_4)_3$ may have to be added.

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SECTION II.

PRECIPITATION OF JAROSITE COMPOUNDS AS A METHOD FOR REMOVING IMPURITIES FROM ACIDIC WASTES FROM CHEMICAL COAL CLEANING

PRECIPITATION OF JAROSITE COMPOUNDS AS A METHOD FOR REMOVING IMPURITIES FROM ACIDIC WASTES FROM CHEMICAL COAL CLEANING

by

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ABSTRACT

Precipitation of jarosite compounds to remove Na, Fe, and SO_4^{2-} from spent acid solutions from a chemical coal cleaning process was studied in relation to reaction time and pH. Although Fe and SO_4^{2-} could be removed effectively from model solutions at pH values of 1.5-2.3, optimum Na removal was possible only within the narrow pH range of 1.4-1.6. Maximum precipitate yields were obtained within about 6 hours at both 80 and 95°C, with at least 80% of the Fe and SO_4^{2-} and about 60-75% of the Na removed. An additional benefit of precipitation of jarosite compounds to remove impurities from spent acid streams is that these compounds have low solubilities in water and are therefore attractive from a waste disposal perspective. Based on this study, the feasibility of spent acid treatment to produce a recyclable feed stream for chemical cleaning of coal has been demonstrated.

INTRODUCTION

Conventional coal cleaning technologies can remove much of the inorganic sulfur in coals by capitalizing on density or surface differences between minerals and coal macerals. However, organic sulfur, which comprises typically 40-60% of the total sulfur in bituminous coals, cannot be removed based on physical properties alone. Thus, chemical treatments are necessary to remove the organic sulfur fraction. While physical cleaning methods have been in use for many years, chemical coal cleaning is still in the developmental stages. The TRW Gravimelt Process, also known as the Molten Caustic Leaching (MCL) Process, is one chemical cleaning procedure that has been studied in detail in recent years (1-7). In the MCL Process, a low-sulfur and low-ash coal is produced in four steps as illustrated in Figure 1. First the coal is leached with molten caustic ($NaOH$ or $NaOH/KOH$ mixture) at 300-400°C for 1 to 3 hours (1-7). Then a series of washing procedures is used on the reacted coal/caustic cake. In the typical sequence of wash solutions, water is followed by a dilute sulfuric acid solution, and then the final step is a water rinse. The acid extract from the first stage of the acid wash section typically contains four weights of water per weight of coal (7). Therefore, from an economic perspective, it is advisable to recycle the spent acid to the acid wash.

The spent acid from the MCL Process contains substantial amounts of Na, Fe, and SO_4^{2-} impurities and may require treatment before it can be recycled back into the cleaning process or discharged to the environment. One option for treating the spent acid stream is to precipitate the impurities as double salts in the jarosite family of

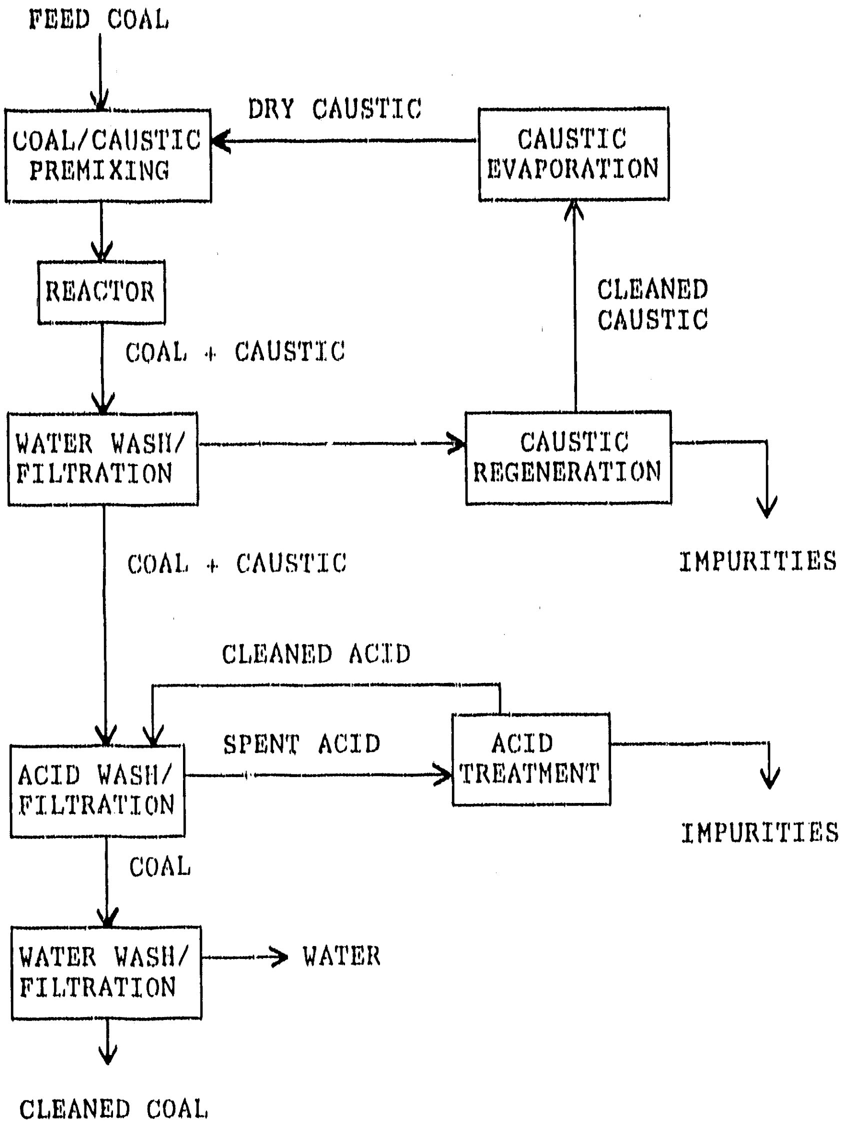

Figure 1. Typical schematic flow diagram for the MCL process

compounds. Jarosite compounds have the theoretical composition: $MFe_3(SO_4)_2(OH)_6$, where "M" is a monovalent cation from the group H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, Tl^+, $1/2Pb^{2+}$, or $1/2Hg^{2+}$ (8,9). Alkali jarosite compounds are crystalline, can be easily dewatered and dried, and may be resistant to leaching, thus providing a stable compound that can be disposed without additional treatment (10).

In this study, the feasibility of removing impurities from acid solutions by precipitation of jarosite ($KFe_3(SO_4)_2(OH)_6$) and natrojarosite ($NaFe_3(SO_4)_2(OH_6)$ was evaluated. The goal of this work was to determine general operating guidelines for precipitating jarosite compounds from spent acid solutions typical of those produced in the MCL Process. Reaction conditions (reaction time, temperature, and pH) necessary for removing Na, Fe, and SO_4^{2-} by formation of natrojarosite were examined. The yield, chemical and mineralogical composition of the precipitate, and the dissolved ions present in the solutions after solid/liquid separation were studied using model solutions.

The results obtained from studies with model solutions were applied to spent acids produced during laboratory countercurrent washing of caustic-treated coal. The major difference in the spent acid from the actual coal cleaning test compared to the model solutions was the presence of K in addition to the Na, Fe, and SO_4^{2-}.

BACKGROUND

Spent acid generated from the MCL Process is expected to contain alkali sulfate concentrations in the range of 2.5-5 g/L and ferric sulfate concentrations around 5-10 g/L (7). The corresponding ion concentrations are 0.8-1.6 g/L of Na, 1.4-2.8 g/L of Fe, and 5.3-10.6 g/L of SO_4^{2-}. Thus, Fe:Na mole ratios are anticipated to range from 0.4 to 1.4. Due to constraints of material durability and practical considerations of process time and temperature, it is desirable for the treatment of spent acid streams to be completed within 12 hours at temperatures no higher than 80°C (11). These constraints of reaction time and temperature, in conjunction with the predicted levels of impurities in the spent acid stream, were used as a basis for this experimental study.

The procedure for precipitating jarosite-type compounds in this study was adapted from the Jarosite Process used in hydrometallurgical processing of Zn (9). In the Jarosite Process, Fe is precipitated from acidic leach solutions by adding a precipitating agent (usually Na^+ or NH_4^+) and then maintaining a pH of about 1.5 while heating the solution to about 95°C (9,12,13). Hydronium ion (H_3O^+) substitutes for a portion of the alkali metal in jarosite compounds (14-16). Thus, although the theoretical composition of jarosite compounds is $MFe_3(SO_4)_2(OH)_6$, the actual composition for most natural and synthetic jarosite compounds is $M_{(1-x)}(H_3O)_xFe_3(SO_4)_2(OH)_6$ where "x" is typically 0.15 to 0.25 (14).

The overall stoichiometry for precipitating natrojarosite is represented by the following reaction (10):

$$3Fe_2(SO_4)_3 + Na_2SO_4 + 12H_2O \longrightarrow 2NaFe_3(SO_4)_2(OH)_6 + 6H_2SO_4$$

The acid that is liberated during the precipitation reactions causes a decrease in pH. For precipitation of jarosite compounds, an initial reaction period is required to form the precursor Fe species. The entire reaction is completed within about 6 hours at 95°C (17). For temperatures ranging from 50 to 95°C, the rate of crystallization is related to the nature of the monovalent cation present, with K^+ more reactive than Na^+ and H_3O^+ (18). Jarosite precipitation is favored both thermodynamically (17,19) and kinetically (18) to formation of natrojarosite.

EXPERIMENTAL METHODS

Experimental Procedures

To determine the effects of time, temperature, and pH on yields of natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), model solutions were formulated using concentrations of Na, Fe, and SO_4^{2-} in ranges typical of the MCL Process spent acid stream. To simplify analytical and experimental aspects of the study, Na was the only alkali metal added to the synthetic solutions.

Reagent-grade H_2SO_4, Na_2SO_4, and $Fe_2(SO_4)_3 \cdot xH_2O$ (ferric sulfate) were used for all of the experiments. The $Fe_2(SO_4)_3 \cdot xH_2O$ was dried at 180°C for about 24 hours in air prior to use and, based on spectrophotometric measurements of Fe, was assumed to be in the monohydrate form. The Na_2SO_4 was dried at 110°C for about 24 hours prior to use. All solid chemicals used for the precipitation experiments were stored in a desiccator.

For these tests, 1.25 g Na_2SO_4 and 14.0 g $Fe_2(SO_4)_3$ were added to 250 mL water. Thus, the starting solutions contained 3.74 g Fe, 0.41 g Na, 10.51 g SO_4^{2-}, and no added Ca. The $Fe_2(SO_4)_3$ concentration was selected to contain an amount of Fe^{3+} that was 25% in excess of the stoichiometric requirement for complete Na removal by precipitation as natrojarosite. The resulting concentrations of Fe^{3+} or $Fe_2(SO_4)_3$ were 15 g/L and 56 g/L, respectively. Thus, excess Fe was available to compensate for any H_3O^+ substitution of the alkali metal in jarosite compounds, while maintaining the availability of Fe for precipitating the Na as natrojarosite. The masses and concentrations of the chemical constituents in the starting solutions are summarized in Table 1.

A schematic diagram of the experimental procedure is shown in Figure 2. All tests were performed as completely-mixed batch studies using covered beakers on hot plates that were stirred continuously at a moderate rate to provide good mixing. To prepare the solutions, distilled water was heated to 40-50^oC and ferric sulfate was added. Following a reaction period of about 15 minutes at this temperature, the Na_2SO_4 was added while maintaining the temperature constant. The pH was then adjusted with H_2SO_4 or $CaCO_3$ and the solution was heated to the desired temperature.

At the end of the reaction period, the precipitates were removed from the liquid phase by vacuum filtration using Gelman GN-6 membrane filters (nominal pore size of 0.45 μ m). After collecting the filtrate for chemical analyses, the precipitates were rinsed extensively with small volumes of distilled water and then air-dried for 1-2 days. The precipitates were characterized by x-ray diffraction and by chemical analyses of dissolved aliquots of the precipitates. Parallel chemical analyses were also performed on the filtrates. The degree of removal of ions from solution as a result of precipitation of jarosite compounds was determined by comparing the composition of the initial solutions to the composition of the filtrates obtained at the end of the reaction period.

Table 1. Initial quantities and concentrations of chemical constituents in the model solutions

	Amount (g)	Concentration (g/L)
Na_2SO_4	1.25	5.00
Na	0.41	1.64
$Fe_2(SO_4)_3$	14.0	56.0
Fe	3.74	15.0
SO_4^{2-}	10.5	42.0
Ca	0.00	0.00

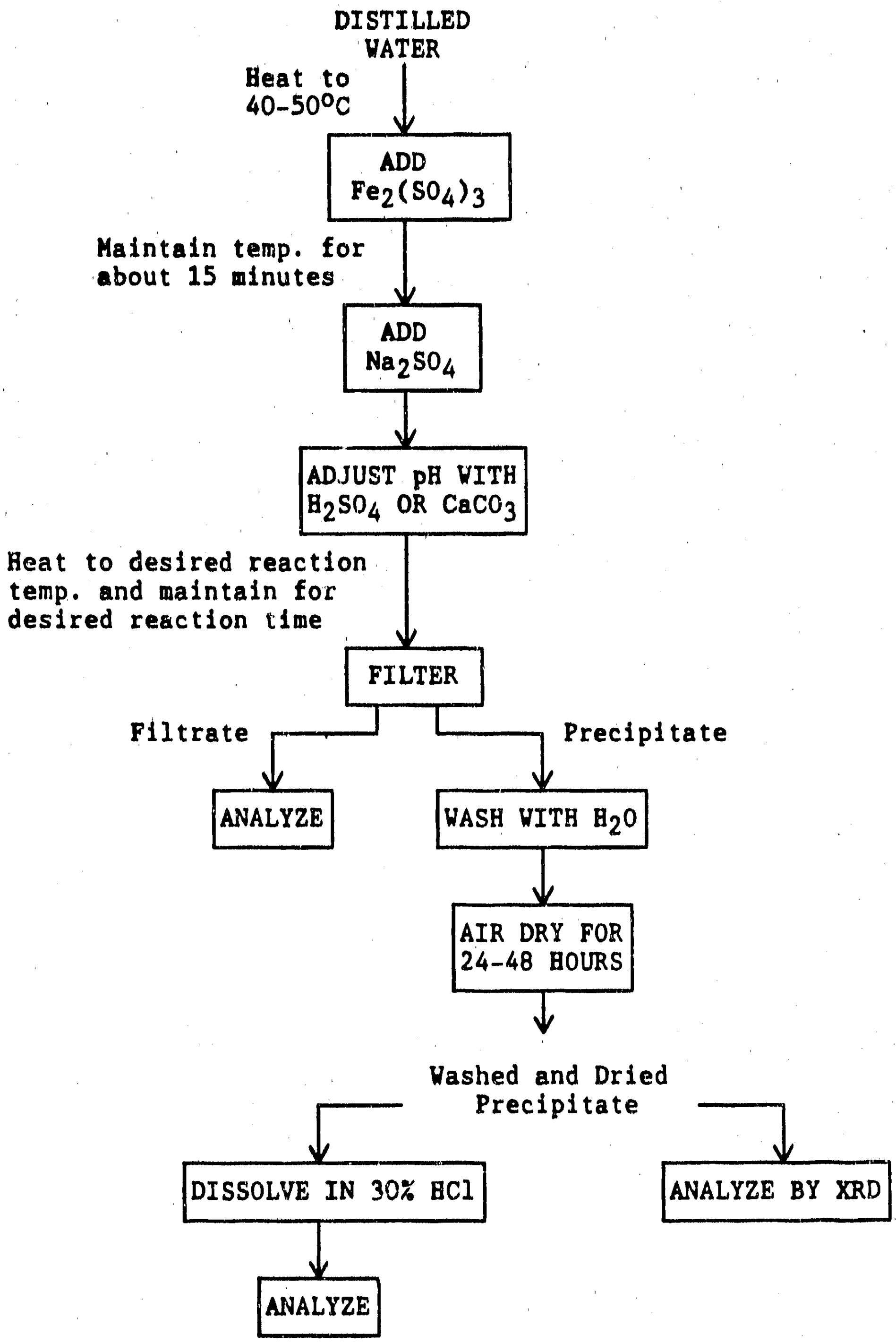

Figure 2. Experimental procedure used in this study

A summary of the experiments performed in this study is presented in Table 2. Tests were performed using reaction times of 1, 3, 6 and 9 hours, temperatures of 80°C and 95°C, and pH values of 1.1, 1.3, 1.4, 1.5, 1.6, 1.7, 1.9, and 2.3. The desired pH values (in the range of 1.1 to 2.3) were maintained during the tests by adding $CaCO_3$ to neutralize H_2SO_4 produced during the precipitation reactions. During the precipitation reactions, the pH was monitored continuously and readjusted to the desired value (using $CaCO_3$) if a deviation of 0.1 pH units occurred. The pH was measured with an Orion Ross Model 815500 Combination pH Electrode and an Altex Model 2000 Ion Analyzer. For measurements at 80°C and 95°C, the temperature-compensation dial on the ion analyzer was used. All the studies on precipitate yield as a function of pH were performed using temperatures of 80°C and reaction times of 6 hours.

For the yield versus time studies, tests were performed for 1, 3, 6, and 9 hours at controlled pH values of 1.5 and 1.7 at temperatures of 80 and 95°C. These pH values were chosen based on results from the study on the effects of pH on the precipitation of natrojarosite. A pH value of 1.7 and a temperature of 95°C (the Jarosite Process is typically run at that temperature) were selected as a basis for comparison of reaction rates and precipitate composition under slightly modified conditions.

To determine whether jarosite compounds could be precipitated effectively from actual spent acid solutions from the MCL Process, a test was also performed at the Ames Laboratory using spent acids produced during bench-scale countercurrent washing of coal which had

Table 2. Summary of experiments performed in this study[a]

Experimental Variable	Time (hours)	Temp. (°C)	pH
pH	6	75-80	1.1-2.3
time	1-9	75-80	1.5
time	1-9	75-80	1.7
time	1-9	95	1.5

[a] All starting solutions contained 1.25 g Na_2SO_4 and 14.0 g $Fe_2(SO_4)_3$ in 250 mL water.

been leached with a molten NaOH/KOH mixture (20). The spent acid solution was treated with 60 g/L of $Fe_2(SO_4)_3$. The added Fe was about half of the theoretical requirement for removing all of the K as jarosite (assuming precipitation of K is necessary before natrojarosite could form). The solution was heated for 6 hours at 75-80°C while maintaining a pH of about 1.5 by using $CaCO_3$. These reaction conditions were derived from results obtained from the experiments with the synthetic acid solutions and in compliance with the temperature restrictions of the pilot-scale reaction tank.

Analytical Procedures

The chemical composition of each precipitate and filtrate was determined. Approximately 1 gram of each precipitate was dissolved in 70 mL of 30% HCl at 60°C on a hot plate/stirrer. The solution was cooled and transferred to a volumetric flask for dilution with distilled water. For experiments in which less than 1 g of precipitate was produced, the final solution volume was scaled back proportionally. Both filtrates and solubilized precipitates were analyzed for Ca, Fe, K, Na, and SO_4^{2-}, while the precipitates were also analyzed for mineralogical composition. The analytical techniques used in this study are summarized briefly in Table 3 and are discussed individually in more detail below.

Ca determinations

Calcium was determined by conventional atomic absorption spectroscopy using standard addition techniques.

Table 3. Analytical methods used in this study

Determination	Analytical Method
Ca	Atomic Absorption
Fe	Spectrophotometry
K	Ion Chromatography
Na	
in filtrates	Ion Chromatography
in precipitates	Atomic Absorption
Sulfate	Ion Chromatography
Mineralogy	X-ray Diffraction

Fe determinations

Acetic acid-ammonium acetate buffer, hydroxylamine-hydrochloride solution, and 1,10-phenanthroline were added to aliquots of the filtrates and dissolved precipitates according to methods described by Chriswell et al. (21). The solutions were diluted with distilled water and allowed to cool for 30 minutes before determining the Fe with a Varian spectrophotometer at a wavelength of 510nm. Duplicate analyses were performed on each sample using two separate sample aliquots. The duplicate analyses were averaged to give the results of the determination. Typically, the results from the duplicate analyses were within ±2% (relative).

K and Na determinations

Filtrates were diluted to the range of 5 to 10 ppm Na or K. Concentrations of these elements were then determined by ion chromatography (IC) using a Dionex 2020i Ion Chromatograph. At least two injections were made for each of the diluted solutions. Replicate analyses of each diluted solution were typically within ±5% (relative); however, different aliquots of the same sample were only reproducible to within ±15% (relative). For analytical comparison, five filtrates from the study of pH versus precipitate yield were analyzed for Na by using both IC and atomic absorption. Results were within ±10% (relative) of each other; deviations ranged from 0.1% to 13%.

For the dissolved precipitates, the K was also determined by IC. However, the Na content of these dissolutions was determined by conventional atomic absorption techniques, using standard addition, since H_3O^+ associated with the HCl used to dissolve the sample interfered with analysis by IC.

SO_4^{2-} determinations

The filtrates and precipitate dissolutions were diluted to produce a SO_4^{2-} concentration of approximately 10 to 20 ppm. The SO_4^{2-} was determined using IC by injecting aliquots of the diluted solutions into a Dionex 2020i Ion Chromatograph anion system. At least two injections were made for each of the diluted solutions. The percent difference between duplicate injections of the same sample was typically less than ±5% (relative).

Mineralogy

The mineralogical composition of the precipitates was determined by x-ray diffraction (XRD) using a Picker theta-theta x-ray diffractometer with Mo K-alpha radiation. Compounds were identified subsequently by comparing the results with standard JCPDS files (22).

RESULTS

Effects of pH in Model Solutions

The ratio of the precipitate yield (in grams) to the total mass of solids ($Fe_2(SO_4)_3$, Na_2SO_4, and $CaCO_3$) added to the solution as a function of pH is shown in Figure 3. The precipitate yield increased dramatically as the pH was increased from 1.1 to about 1.5. At pH values greater than or equal to 1.5, over 90% of the solids added to the solution were precipitated as natrojarosite and gypsum ($CaSO_4 \cdot 2H_2O$) within 6 hours at 80°C.

To determine if the increase in precipitate yield was due primarily to the addition of $CaCO_3$ or to solution chemistry, the precipitate yield was compared to the quantity of $CaCO_3$ added as a function of pH in Figure 4. The $CaCO_3$ added was linearly related to pH, unlike the precipitate yield which increased markedly between pH 1.2 and 1.5. Since above pH 1.5 the two curves appear nearly parallel, the quantity of $CaCO_3$ added did not seem to control the precipitate yield under these test condtions.

Removals of Fe, Na, and SO_4^{2-} from the acid solutions as a function of pH are shown in Figure 5 (see Appendix IV for all experimental data). Duplicate runs were performed at some of the pH values. For clarity, results from duplicate runs were averaged and the average values were plotted. For these tests, removals of Fe and SO_4^{2-} were reproducible to within $\pm$5% (relative). The Na removals were generally reproducible to within $\pm$10% (relative) or less, except at pH 1.7 where Na removal varied by as much as 30% (relative) from the mean. The pH value of 1.7 appears

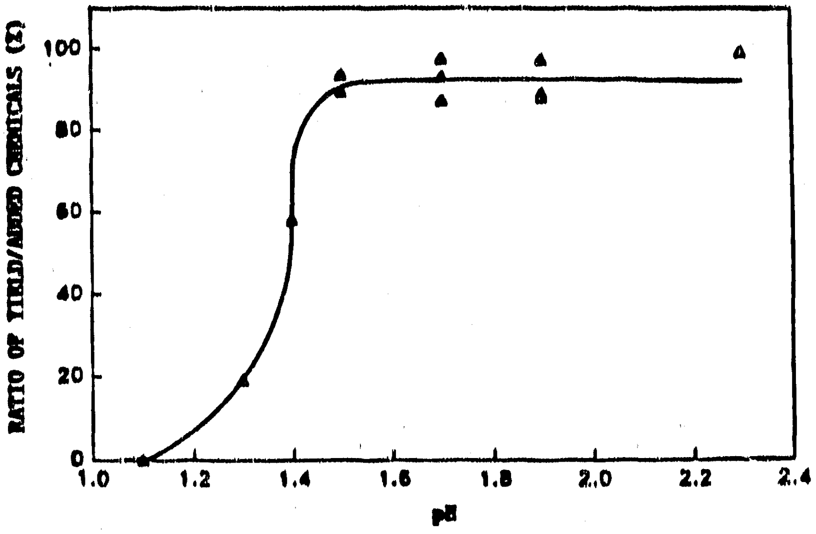

Figure 3. Ratio of precipitate yield (grams) to total grams of solids ($Fe_2(SO_4)_3$, Na_2SO_4, and $CaCO_3$) added

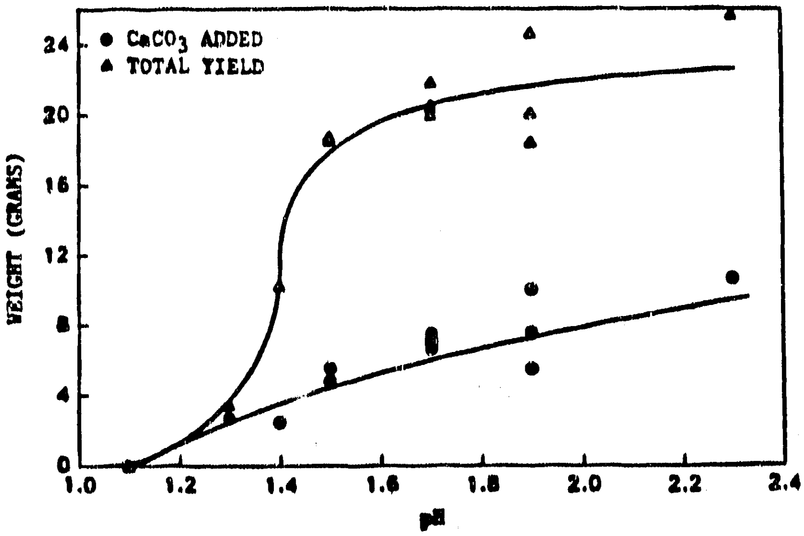

Figure 4. Precipitate yield (grams) and $CaCO_3$ (grams) added as a function of pH

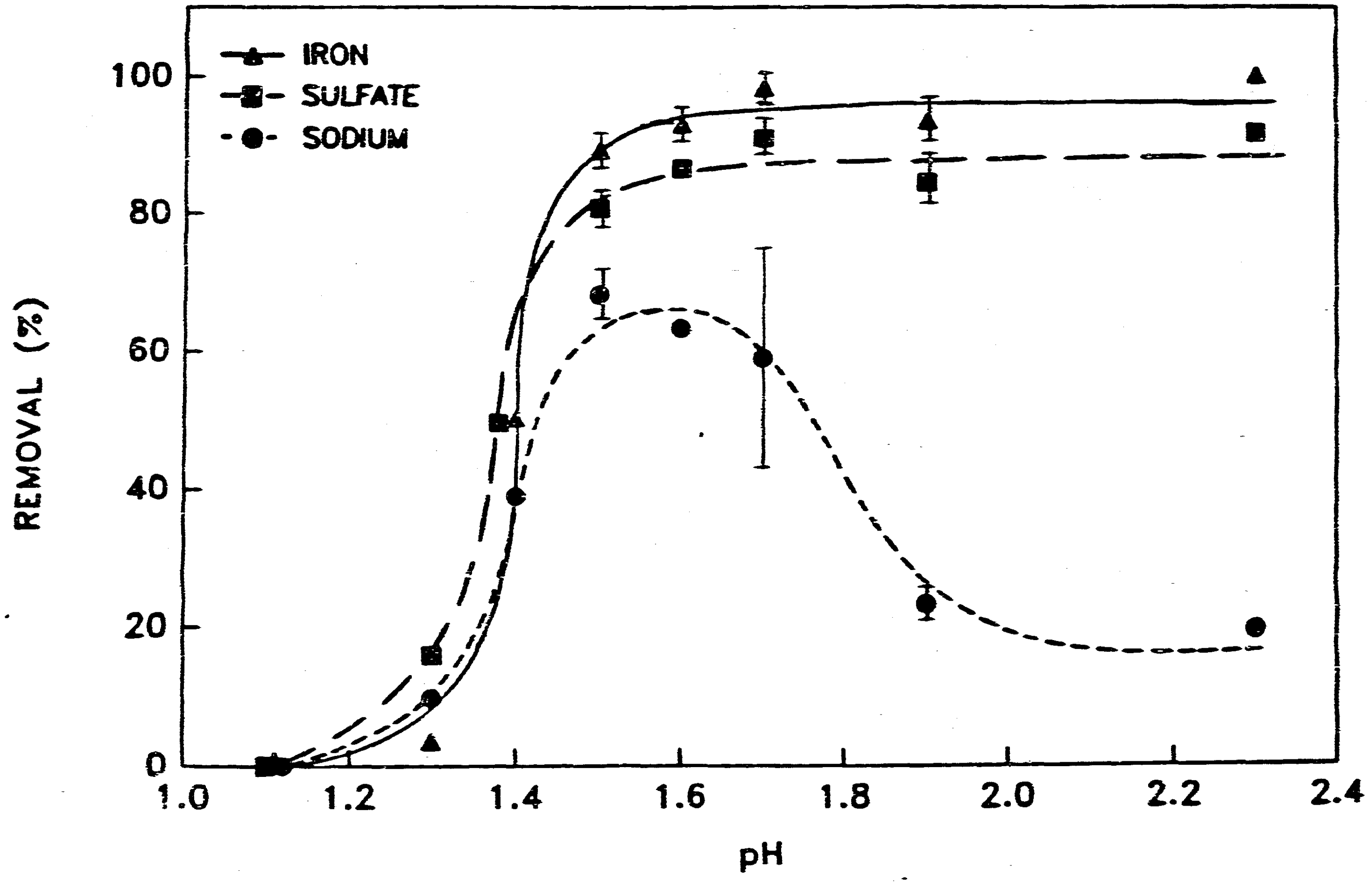

Figure 5. Iron, sulfate, and sodium removal as a function of pH; solutions were heated at 75-80°C for 6 hours; error bars represent ± one standard deviation from the mean

to be critical for natrojarosite formation, and even small deviations from this pH can influence precipitate formation dramatically.

The removal of Fe and SO_4^{2-} as a function of pH was consistent with results of precipitate formation (see Figure 3), with higher Fe and SO_4^{2-} removal observed at pH values of about 1.1 to 1.5. Overall, about 90% of the Fe and SO_4^{2-} were removed at pH 1.5. The trend for Na removal differed from that for Fe and SO_4^{2-} removal in that the maximum removal occurred at about pH 1.6. As can be seen, maximum Na removals of only 65-70% were obtained, even though the initial Fe concentration in the solution was 25% in excess of the theoretical requirements for complete precipitation of Na as natrojarosite. Significant amounts of Na were precipitated at pH values of about 1.4 to 1.7, while little or no Na was removed at pH values outside of this range.

XRD analyses on the precipitates indicated that both natrojarosite and gypsum were formed in the pH range of 1.4 to 1.7, while gypsum was the primary component of precipitates obtained outside of this pH range. These data are consistent with optimum Na removal as determined from chemical analyses of filtrates. No other mineral species were identified in any of the precipitates. At a pH of 1.1, the major component of the precipitate was gypsum, but SO_4^{2-} ions in the acid solutions were not depleted substantially because of the low precipitate yield. At pH 1.4, the precipitate yield was higher, and significant quantities of both natrojarosite and gypsum were formed. Maximum yields occurred at pH values of 1.5 and 1.7, and substantial amounts of Fe and SO_4^{2-} were removed as natrojarosite and gypsum.

At pH values of 1.9 and 2.3 little or no natrojarosite was formed; however, the removal of both Fe and SO_4^{2-} remained high. The SO_4^{2-} was precipitated as gypsum, but no Fe-bearing phases were detected by XRD. However, due to the orange tint of precipitates formed at pH values above 1.9, it is believed that amorphous Fe compounds were precipitated at those pH values. Such compounds would not produce well-defined peaks in the XRD spectrum. The presence of amorphous compounds is supported by the fact that XRD peak intensities observed for those precipitates were significantly less than those obtained for samples of pure gypsum, suggesting that significant amounts of amorphous material may be present. In addition, when these precipitates were dissolved in acid and analyzed for Fe by spectrophotometry, it was determined that about 15% of the mass of the precipitate was comprised of Fe.

Results of the Fe, Na, Ca, and SO_4^{2-} analyses on the dissolved precipitates are shown in Table 4. The sensitivity of natrojarosite precipitation to pH and the difficulty in maintaining precise pH values during these tests influenced the reproducibility of experimental results. However, the general trends were consistent and there was good agreement between chemical data from the analyses of both filtrates and precipitates and from mineralogical data on the precipitates. For example, the precipitate from the test performed at pH 1.3 contained mostly Ca and SO_4^{2-}, which was confirmed by XRD data that identified gypsum ($CaSO_4 \cdot 2H_2O$) as the predominant mineral formed at that pH value. The optimum removal of Na at pH 1.5 was confirmed by analyses of filtrate, solid, and precipitate dissolution. Also, the high Fe:Na mole ratios at pH values above 1.7 provide evidence that at those pH values

Table 4. Precipitate composition as a function of pH[a]

	Weight Percent in Precipitate				Molar Ratios	
pH	Fe	SO_4^{2-}	Na	Ca	Fe:Na	Ca:Na
1.3	0.89	57.9	0.04	23.3	9.16	334
1.4	21.8	46.3	1.68	11.6	5.35	3.96
1.5	18.3	51.0	1.46	9.04	5.14	3.55
1.5	18.7	48.3	1.40	11.0	5.49	4.50
1.6	17.7	48.7	1.24	10.9	5.87	5.05
1.7	17.4	48.0	1.00	12.5	7.17	7.18
1.7	17.1	47.9	1.32	11.4	5.34	4.96
1.7	17.2	49.3	1.46	11.0	4.86	4.31
1.7	17.2	45.4	0.82	12.7	8.64	8.89
1.7	17.2	42.5	0.50	13.5	14.1	15.5
1.9	14.6	54.7	0.20	11.9	30.0	34.0
1.9	17.3	45.1	0.12	14.4	59.5	69.0
2.3	14.2	43.7	0.04	15.7	146	225

[a] Solutions heated at 75-80°C for 6 hours.

the Fe was precipitated as some compound other than natrojarosite. The Ca:Na mole ratios are an indication of the relative amounts of gypsum and natrojarosite in the precipitates. Based on these experimental results, virtually no natrojarosite formed outside of the pH range from 1.4 to 1.7.

Effects of Reaction Time on Precipitating Jarosite Compounds from Synthetic Solutions

Precipitate weights and the amount of $CaCO_3$ added to the solution (for pH adjustment) as a function of reaction time are shown in Figure 6. These results demonstrate that the yield was not dependent on the increased amounts of $CaCO_3$ added at the longer reaction times. At pH 1.5, maximum precipitate yields were obtained within 6 hours at both 80°C and 95°C. However, at 95°C the reaction rates were higher than at 80°C. The influence of pH on reaction rate can be seen by comparing Figures 6B and 6C. At pH 1.7, maximum yields were obtained within 3 hours.

Removals of Fe, Na, and SO_4^{2-} from the synthetic solutions as a function of time for all of the reaction conditions studied are summarized in Figure 7 (see Appendix IV for all experimental data). At least 80% of the Fe and SO_4^{2-} and 60-75% of the Na were precipitated after about 6 hours. A pH of 1.5 appeared to be slightly more effective at removing Na than a pH of 1.7. Natrojarosite and gypsum were the only mineral phases identified by XRD in any of the precipitates.

Results of the chemical analyses on the precipitate dissolutions from these tests are shown in Table 5. After a reaction time of 1 hour,

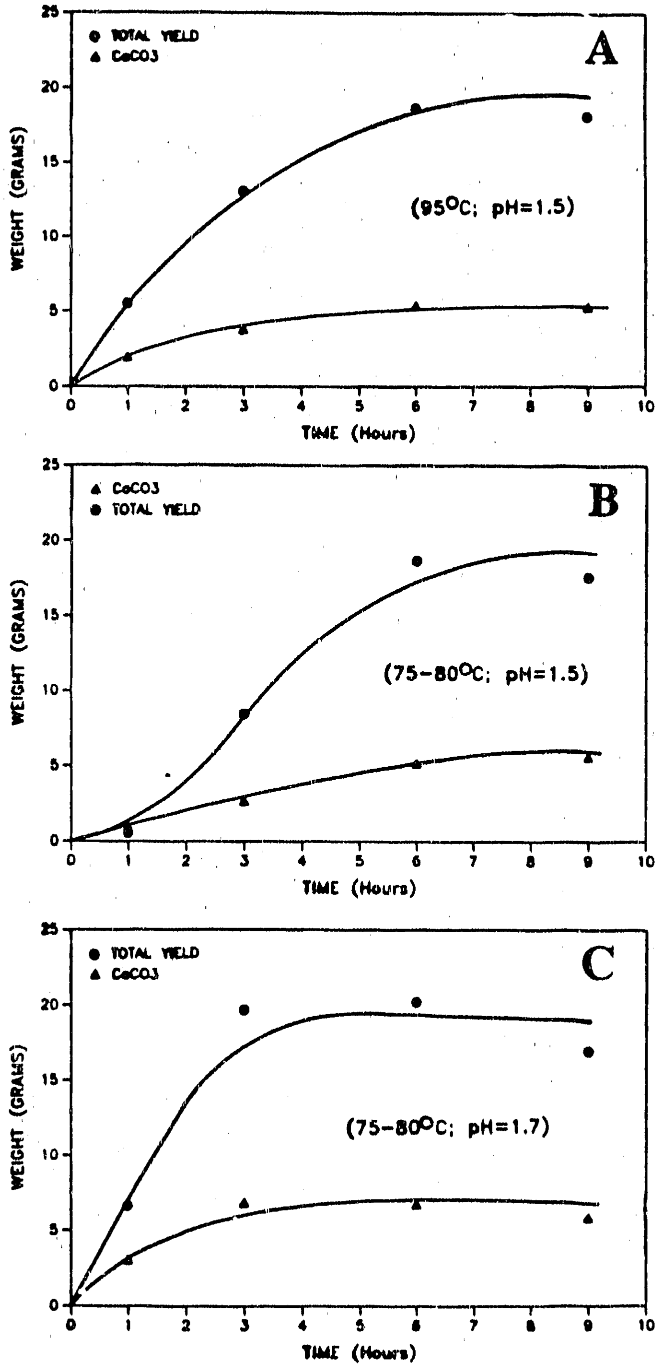

Figure 6. Precipitate yield (grams) and $CaCO_3$ (grams) added as a function of time at various temperatures and pH values

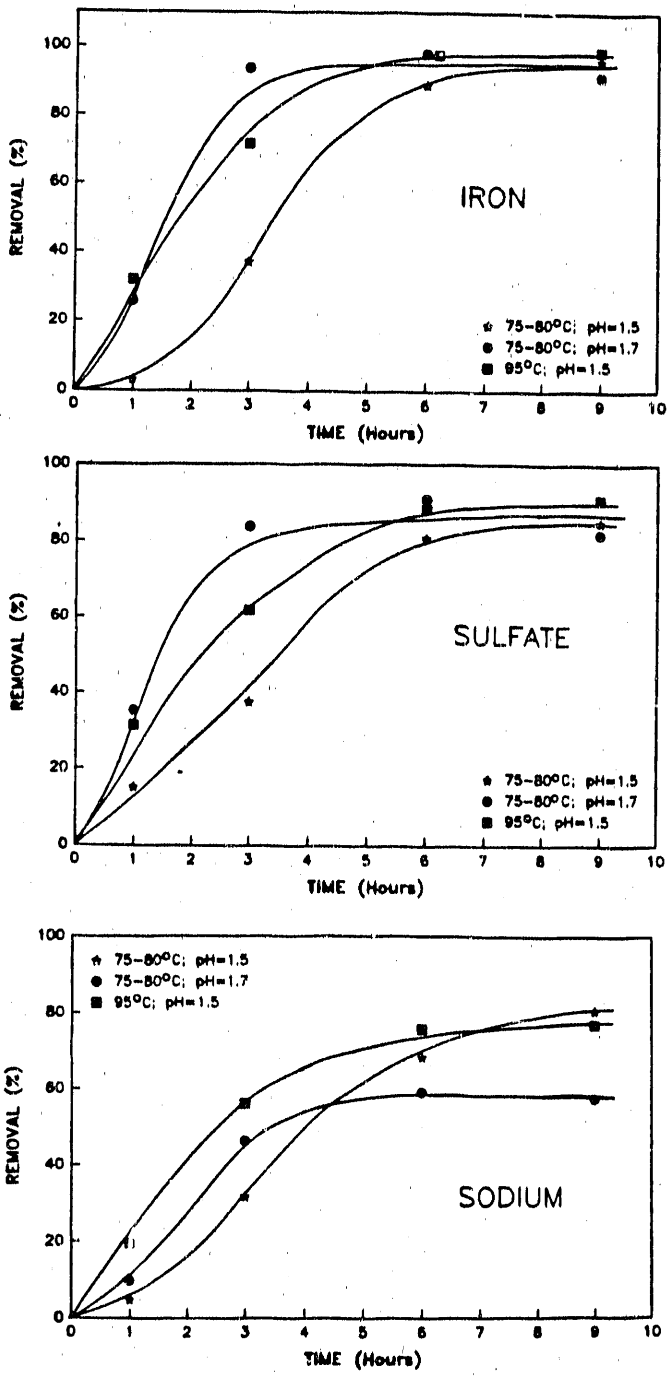

Figure 7. Removal of iron, sulfate, and sodium as a function of reaction time at various temperatures and pH values

Table 5. Precipitate composition as a function of reaction time[a]

Reaction Time (hrs)	Precipitate Composition				Fe : Na Ratio (molar)	Ca : Na Ratio (molar)
	%Fe	$\%SO_4$	%Na	%Ca		
1	10.4	53.4	0.74	16.3	5.78	12.6
1	6.47	51.1	0.14	19.8	19.0	81.0
3	17.8	50.3	1.38	10.8	5.31	4.40
6	18.3	51.0	1.46	9.04	5.14	3.55
6	18.7	48.3	1.40	11.0	5.49	4.50
9	19.5	48.0	1.70	9.99	4.72	3.37

[a] Solutions heated at 75-80°C while maintaining a pH value of 1.5 by adding $CaCO_3$.

concentrations of Fe and Na were lower and concentrations of Ca were higher as compared to the composition of precipitates obtained after longer reaction times. These results reflect the initial reaction period necessary for forming the intermediate chemical species required for natrojarosite formation. The initial precipitates are predominantly gypsum and contain little natrojarosite.

Tests with Spent Acid from Washings of Chemically Cleaned Coal

Spent acids produced from countercurrent washing of caustic-cleaned coal required the addition of 6.82 g of $CaCO_3$ during heating to maintain the desired pH of 1.5, and yielded 22.6 g of precipitate (dry). Results of chemical analyses on the initial solution, the filtrate at the end of the test, and the precipitate dissolution are presented in Table 6. As predicted by the studies on double salt precipitation using model compounds, Fe, SO_4^{2-}, and alkali metals were effectively precipitated as jarosite compounds ($(K,Na)Fe_3(SO_4)_2(OH)_6$) and gypsum by heating the solution at about 80°C for 6 hours while maintaining a pH value of 1.5 with $CaCO_3$. Chemical and XRD analyses indicated jarosite was the predominant jarosite species formed from the spent acid solution at pH 1.5. These results are consistent with the kinetic and thermodynamic theories (17-19) that jarosite forms preferentially over natrojarosite.

Table 6. Comparison of spent acid solution composition before and after precipitation[a]

	K(g)	Na(g)	Fe(g)	SO_4(g)	Ca(g)
Solution[b]					
Before precipitation[c]	1.61	1.41	0.80	12	0.07
After precipitation	0.65	1.10	0.41	8	0.07
	K(%)	Na(%)	Fe(%)	SO_4(%)	Ca(%)
Precipitate	3.81	0.12	15.0	50.9	11.7

[a] Spent acid was produced from laboratory countercurrent washing of caustic-treated coal.

[b] Initial volume used for test was 200 mL.

[c] Prior to addition of additional Fe as $Fe_2(SO_4)_3$.

Mass Balances

To evaluate the effectiveness of the experimental and analytical procedures used in this study for quantifying removal of impurities from acid solutions, mass balances were calculated for representative tests. When pH was varied in model solutions, the total amounts of Fe and SO_4^{2-} detected in filtrates and precipitates were typically within ±5% of the initial quantity of Fe and SO_4^{2-} in the starting solution. The Na mass balance was within ±10-20%. For the tests in which reaction time was varied, Na and Fe mass balances were within ±5% of the initial amounts in solution. For SO_4^{2-}, mass balances were within ±5%-15%. For the test with the spent acid solution, mass balances agreed to within ±5% for K, Fe, and SO_4^{2-}, but agreed only to within ±20% for the Na.

The inconsistencies in the mass balances may be due to either analytical or sampling errors. The importance of analyzing both liquid and solid phases independently is demonstrated by the results from these experimental studies. Each analytical method has limitations; however, by careful combination of analytical methods, a more realistic analysis of the process can be derived.

SUMMARY AND CONCLUSIONS

Precipitation of natrojarosite is an effective means for removing Fe, SO_4^{2-}, and Na from spent acid solutions. Because substantial amounts of the major impurities were removed, the spent acid should be able to be recycled for acid washing during coal cleaning, particularly for the MCL Process, and precipitation reactions can be completed within 12 hours at 80°C. Under the conditions studied, the effective pH range for precipitating jarosite compounds from acid solutions appeared to be very narrow, with an optimum pH of about 1.5 ± 0.1. For reaction periods of about 6 to 12 hours, the chemical composition of the precipitate was constant. For the spent acid sample, which contained both Na and K, jarosite precipitated preferentially to natrojarosite, and K, Fe, and SO_4^{2-} impurities were effectively precipitated as jarosite and gypsum at pH 1.5 and 80°C. For both the model solutions and the laboratory-generated spent acids, the ratio of alkali metals to Fe in the initial solutions were too low and therefore it was necessary to increase the Fe concentration substantially by adding $Fe_2(SO_4)_3$.

The technical feasibility of jarosite precipitation as a method for treating acidic waste streams typical of the MCL Process was demonstrated in this project. A detailed analysis of the economic feasibility is necessary before any scale-up work can be conducted. Also, more economical methods of increasing the Fe content of the solution should be evaluated. The mole ratios of Fe to alkali metals present in the spent acid solutions will influence the amount of Fe needed for the reaction. More accurate estimates of these ratios will be obtained as the chemical coal-cleaning technology of the MCL Process is further developed.

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SUMMARY AND DISCUSSION

Results obtained with model solutions and spent acid from a laboratory simulation of countercurrent washing of caustic-treated coal indicate that precipitation of jarosite compounds from such solutions is technically feasible. The solution pH is the most critical factor governing precipitation of these compounds under the conditions studied. A pH of 1.4 to 1.6 should be maintained during precipitation. Because of this narrow pH range, the pH will have to be carefully monitored in plant operations. To precipitate Na as natrojarosite, a neutralizing agent will be required, since acid is released during the precipitation reactions. At temperatures of 80 to 95°C, precipitation is essentially complete within six hours.

Precipitation of jarosite compounds removed 95% or more of the Fe and K, 80 to 90% of the sulfate, and 70 to 80% of the Na. This degree of removal is adequate for recycling the spent acid. Removal of the Na as natrojarosite is hindered by hydronium ion substitution for the alkali metal. In cases where both K and Na are present, removal of the Na will be complicated by the fact that jarosite precipitates preferentially to natrojarosite.

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APPENDIX I -- EXPERIMENTAL PROCEDURES

This appendix describes the experimental procedures used in this study.

1. Dry reagent-grade Na_2SO_4 at 110°C for several hours and store in desiccator in a capped jar.

2. Place reagent-grade $Fe_2(SO_4)_3 \cdot xH_2O$ in large petri dishes or other suitable containers and spread to thickness of about 1/4 inch. Place the open containers in a vacuum drying oven and dry the ferric sulfate for about 24 hours at 180°C. Do not have a vacuum on the oven chamber, but maintain a continuous dry air purge (arbitrary flow) through the oven to remove acidic vapors and moisture from the oven. Vent these vapors into an exhaust hood. Store the dry $Fe_2(SO_4)_3$ in a capped jar in a desiccator.

3. Measure desired amount of distilled water with a graduated cylinder and pour water into beaker of an appropriate size.

4. Place beaker on hot plate/stirrer and stir continuously using a magnetic stirring bar at an intermediate rate (arbitrary). The stirring rate is not crucial, but should be adequate to provide good mixing and maintain much of the precipitate in suspension.

5. If a specific initial pH is desired, acidify the water at this point using a dilute (10-30%) H_2SO_4 solution.

6. Heat water to 40-50°C, then add all of the $Fe_2(SO_4)_3$ (weighed out to the nearest 0.1 g).

7. Maintain temperature for about 15 minutes, or until solution is no longer cloudy.

8. Add all of the Na_2SO_4 (weighed out to nearest 0.1 g) and allow to dissolve.

9. If a constant pH is desired throughout the test, add either H_2SO_4 or $CaCO_3$ at this point to acheive the desired pH.

10. Cover beaker with petri dish, watch glass, or other suitable material to minimize evaporative losses. Keep thermometer in the solution at all times by angling the thermometer to set in the spout of the beaker.

11. Heat to desired reaction temperature and maintain for the desired reaction time.

12. If a "constant" pH is desired throughout the test, check the pH (temperature-compensated) every 5 - 15 minutes and add $CaCO_3$ as needed (pH will decrease during precipitation). Do not allow pH to deviate by more than 0.1 pH units from the desired pH.

13. At the end of the test, remove the beaker and allow it to stand until the precipitate has settled (typically several minutes). Remove the stirring bar before all of the precipitate settles.

14. Using a Gelman Magnetic Filter Funnel with an Erlenmeyer flask and a water aspirator, filter the precipitate on Gelman GN-6 membrane filters (nominal pore size of 0.45 microns). Decant as much of the liquid into the filter funnel as possible (some of the precipitate will also be transferred).

15. Collect the filtrate and retain for analysis.

16. Sluice precipitate from beaker with distilled water and filter.

17. Wash precipitate at least ten times with small increments of distilled water, with each increment just covering the surface of the filter cake. If there is a large volume of precipitate, it may be necessary to do the filtration in two or three batches. If so, combine all of the filter cakes.

18. Remove filter cakes and spread to a thickness of 1/4" or less.

19. Allow precipitate to air dry for 1 - 2 days at ambient temperature. Store dry precipitate in capped jar.

20. Clean beaker and thermometer with steel wool or hot 10% HCl.

APPENDIX II -- ANALYTICAL METHODS

X-Ray Diffraction

1. Break up any lumps in the sample. Grinding should not be necessary.

2. Mount sample using routine procedures. For this study, the sample (in the form of a powder) was poured into an aluminum tray and leveled off with a glass slide or razor blade by scraping across the top of the sample holder.

3. For x-ray diffraction analyses using a Mo radiation source, scan sample from 2 - 30° two-theta using increments of 0.05° two-theta and counting times of 1 - 5 seconds per step.

4. Compare experimental "d" values with those in standard JCPDS files.

Ion Chromatography

Filtrates

1. Dilute solutions with deionized water so that they contain about 10 - 20 ppm SO_4^{2-} (for sulfate analysis) or 5 - 10 ppm Na or K (for Na and K analyses).

2. Inject aliquots of the diluted solutions directly into the ion chromatograph. Make at least two injections per sample and average the values to get the results of the determination.

Precipitates

1. Dissolve about 1 g of precipitate in 70 mL of 30% HCl at 60°C on a hot plate. This takes about 15 minutes.

2. Cool solution, transfer to a volumetric flask, and dilute to 200 mL with deionized water.

3. Analyze in the same manner as the filtrates.

Atomic Absorption

1. For calcium, dilute the solutions so they contain <2.5 ppm calcium. Determine the calcium by atomic absorption using a nitrous oxide flame by comparing results with those obtained using commercially available atomic absorption standard solutions.

2. For sodium, dilute the solution so they contain <1 ppm sodium. Determine the sodium using an air-acetylene flame by comparing results with those obtained using commercially available atomic absorption standard solutions.

Spectrophotometry

1. Prepare acetic acid ammonium acetate buffer by adding 700 mL glacial acetic acid to a solution of 250 g ammonium acetate in 150 mL distilled water.
2. Prepare 1,10-phenanthroline solution by dissolving 100 mg 1,10-phenanthroline monohydrate in 100 mL distilled water containing two drops of concentrated hydrochloric acid.
3. Prepare hydroxylamine hydrochloride solution by dissolving 60 g hydroxylamine hydrochloride solution in 100 mL of distilled water.
4. Prepare stock iron solution by dissolving 1.404 g of ferrous ammonium sulfate hexahydrate in about 50 mL of 40% (v/v) sulfuric acid, then dilute the solution to exactly 1 liter using demineralized water to yield a stock solution containing 200 ppm iron.
5. Prepare standard iron solution by diluting a 50.00 mL aliquot of stock iron solution to the mark in a 1-liter standard flask with demineralized water to yield a solution containing 10 ppm iron.
6. For sample analysis, pipette two volumes of the sample, estimated to contain between 50 and 150 µg iron each, into two separate 50-mL volumetric flasks.
7. Add 10 mL of the acetic acid-ammonium acetate buffer to each flask.
8. Add 5 mL of hydroxylamine-hydrochloride solution to each flask.
9. Add 3 mL of 1,10-phenanthroline solution to each flask.
10. Dilute the solutions to the mark on the volumetric flask with distilled water and allow to stand for 30 minutes.
11. Determine the absorption of the solution at a wavelength of 510 nm with the spectrophotometer.
12. Quantify the iron concentration by comparing the absorption values to a calibration curve prepared with the standard iron solutions.
13. For each sample, average the results from each of the two sample aliquots to obtain the results of the analysis.

APPENDIX III -- EXPERIMENTAL DATA FROM PRELIMINARY STUDIES OF JAROSITE PRECIPITATION (SECTION I)

Effect of Temperature and Initial pH on Precipitate Yield and Removal of Fe and Na (Table 2 in Section I)[1]

Temp.	Initial	Ppt. Yield	Fe (grams)		Na (grams)	
(°C)	pH	(grams)	Initial	final	initial	final
95	2.70	1.422	0.988	0.200	0.405	0.349
95	2.40	1.383	0.988	0.224	0.405	0.361
95	2.10	1.211	0.988	0.321	0.405	0.339
95	1.80	1.178	0.988	0.417	0.405	0.324
95	1.50	0.238	0.988	0.906	0.405	0.332
80	2.70	0.981	0.988	0.503	0.405	0.367
80	2.40	0.816	0.988	0.607	0.405	0.355
80	2.10	0.892	0.988	0.581	0.405	0.330
80	1.80	0.163	0.988	0.835	0.405	0.328
80	1.50	0.000	0.988	0.919	0.405	0.369
70	2.70	0.393	0.988	0.459	0.405	0.350
70	2.40	0.391	0.988	0.447	0.405	0.357
70	2.10	0.078	0.988	0.906	0.405	0.376
70	1.80	0.005	0.988	0.857	0.405	0.352
60	2.70	0.011	0.988	0.888	0.405	0.367
60	2.40	0.006	0.988	0.983	0.405	0.390
60	2.10	0.000	0.988	0.947	0.405	0.389
60	1.80	0.000	0.988	0.961	0.405	0.364

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[1] Initial amounts of Fe and Na are theoretical amounts based on known quantities of the added chemicals.

Effect of Initial pH and Fe Concentration on Precipitate Yield and Removal of Fe and Na (Table 3 in Section I)[1]

Temp. (°C)	Initial pH	Ppt. Yield (grams)	Fe (grams)		Na (grams)	
			initial	final	initial	final
95	1.80	1.178	0.988	0.417	0.405	0.324
95	1.80	2.114	2.965	2.146	0.405	0.293
95	1.80	5.107	2.965	1.082	1.215	0.951
95	2.40	1.383	0.988	0.224	0.405	0.361
95	2.40	3.319	2.965	1.732	0.405	0.313
95	2.70	1.422	0.988	0.200	0.405	0.349
95	2.70	4.101	2.965	1.499	0.405	0.294

[1] Initial amounts of Fe and Na are theoretical amounts based on known quantities of the added chemicals.

Effect of Temperature and Initial pH on Precipitate Yield and Removal of Fe, Na, K, and SO_4^{2-} (Table 5 in Section I)[1]

Temp. (°C)	Init. pH	Precip. (grams)	Fe (g)		Na (g)		K (g)		SO_4^{2-} (g)	
			init.	final	init.	final	init.	final	init.	final
95	4.00	3.275	1.48	0.38	0.10	0.06	0.14	0.00	4.21	2.72
80	4.00	2.469	1.48	0.68	0.10	0.08	0.14	<0.01	4.21	3.16
95	1.80	2.971	1.48	0.52	0.10	0.07	0.14	0.00	4.21	3.24
80	1.80	2.402	1.48	0.72	0.10	0.09	0.14	<0.01	4.21	3.59
95	4.00	4.314	1.48	0.10	0.00	0.00	0.28	0.01	4.21	n.m.[2]

[1] Initial amounts of Fe, Na, K, and SO_4^{2-} are theoretical amounts based on known quantities of the added chemicals.

[2] n.m. - not measured.

APPENDIX IV -- EXPERIMENTAL DATA FROM STUDIES OF JAROSITE PRECIPITATION USING ACID NEUTRALIZATION (SECTION II)

Precipitate Yield and Removal of Fe, Na, and SO_4^{2-} as a Function of pH (Figure 5 in Section II)[1,2]

pH	Precip. (grams)	Fe (g)		Na (g)		SO_4^{2-} (g)	
		initial	final	initial	final	initial	final
1.1	0.00	3.74	3.88	0.41	0.41	10.51	>10.6
1.3	3.43	3.74	3.61	0.41	0.37	10.51	8.84
1.4	10.30	3.74	1.86	0.41	0.25	10.51	5.29
1.5	18.59	3.74	0.44	0.41	0.12	10.51	2.10
1.5	18.77	3.74	0.37	0.41	0.14	10.51	1.96
1.6	18.40	3.74	0.26	0.41	0.15	10.51	1.41
1.7	21.87	3.74	0.01	0.41	0.15	10.51	0.67
1.7	20.39	3.74	0.03	0.41	0.09	10.51	0.72
1.7	18.16	3.74	0.14	0.41	0.10	10.51	1.10
1.7	20.02	3.74	0.05	0.41	0.20	10.51	1.12
1.7	20.59	3.74	0.07	0.41	0.24	10.51	1.23
1.9	24.67	3.74	0.16	0.41	0.31	10.51	1.39
1.9	20.15	3.74	0.33	0.41	0.32	10.51	1.87
2.3	25.69	3.74	0.00	0.41	0.33	10.51	0.88

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[1] Reactions performed at 75-80°C for 6 hours.

[2] Initial amounts of Fe, Na, and SO_4^{2-} are theoretical amounts based on known quantities of the added chemicals.

Removal of Fe, Na, and SO_4^{2-} as a Function of Reaction Time and pH at 75-80°C (Figure 7 in Section II)[1]

	Time	Precip.	Fe (g)		Na (g)		SO_4^{2-} (g)	
pH	(hrs)	(grams)	initial	final	initial	final	initial	final
1.5	1	0.42	3.74	3.74	0.41	0.39	10.51	9.12
1.5	1	0.68	3.74	3.50	0.41	0.39	10.51	8.71
1.5	3	8.47	3.74	2.35	0.41	0.28	10.51	6.56
1.5	6	18.59	3.74	0.44	0.41	0.12	10.51	2.10
1.5	6	18.77	3.74	0.37	0.41	0.14	10.51	1.96
1.5	9	17.60	3.74	0.14	0.41	0.08	10.51	1.58
1.7	1	6.68	3.74	2.77	0.41	0.37	10.51	6.80
1.7	3	18.58	3.74	0.31	0.41	0.13	10.51	1.66
1.7	3	20.80	3.74	0.16	0.41	0.31	10.51	1.76
1.7	6	21.87	3.74	0.01	0.41	0.15	10.51	0.67
1.7	6	20.39	3.74	0.03	0.41	0.09	10.51	0.72
1.7	6	18.16	3.74	0.14	0.41	0.10	10.51	1.10
1.7	6	20.02	3.74	0.05	0.41	0.20	10.51	1.12
1.7	6	20.59	3.74	0.07	0.41	0.24	10.51	1.23
1.7	9	17.33	3.74	0.31	0.41	0.11	10.51	1.94
1.7	9	16.60	3.74	0.31	0.41	0.24	10.51	1.89

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[1] Initial amounts of Fe, Na, and SO_4^{2-} are theoretical amounts based on known quantities of the added chemicals.

Removal of Fe, Na, and SO_4^{2-} as a Function of Reaction Time and pH at 95°C (Figure 7 in Section II)[1]

pH	Time (hrs)	Precip. (grams)	Fe (g)		Na (g)		SO_4^{2-} (g)	
			initial	final	initial	final	initial	final
1.5	1	4.17	3.74	2.72	0.41	0.34	10.51	7.26
1.5	1	6.88	3.74	2.36	0.41	0.32	10.51	7.16
1.5	3	13.07	3.74	1.06	0.41	0.18	10.51	4.03
1.5	6	18.68	3.74	0.08	0.41	0.10	10.51	1.23
1.5	9	18.68	3.74	0.07	0.41	0.09	10.51	1.11
1.5	9	17.60	3.74	0.01	0.41	0.10	10.51	0.83

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[1] Initial amounts of Fe, Na, and SO_4^{2-} are theoretical amounts based on known quantities of the added chemicals.

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