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SYNTHESIS, CHARACTERIZATION, AND TESTING OF A SULFIDE-SELECTIVE FLOCCULANT

by

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ABSTRACT

The objective of this research project was to investigate the feasibility of the synthesis of a new sulfide-selective flocculant (PVX-2000).

As is known in froth flotation practice, xanthate containing reagents, are taken up by sulfide minerals; therefore, if a xanthate group could be incorporated into the structure of a long chain polymer such as polyvinyl alcohol, selective polyvinyl xanthate (PVX-2000), a flocculant selective to sulfide minerals, might be obtained.

Experimental investigation reported in this work confirmed this possibility. The reaction was confirmed by ultraviolet and infrared spectroscopy techniques.

Flocculation studies on single and mixed mineral systems (chalcopyrite, pyrite, galena, quartz) were conducted using the PVX-2000 synthesized. The effect of pH and PVX-2000 concentration were also investigated in this study. It was confirmed that the product obtained is selective towards pyrite, chalcopyrite and galena, at certain pH values, while it had no flocculation action on quartz suspension.

Separation tests were conducted on synthetic mixtures of mineral slimes on the basis of test results obtained using single mineral suspension.

Separation of pyrite from its mixture with quartz was achieved. Results obtained suggest that separation of galena/pyrite, galena/chalcopyrite mixtures by selective flocculation is possible using synthesized PVX-2000.

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I. INTRODUCTION

The problem of beneficiation of mineral fines has been recognized for sometime, but it has recently become more significant due to the disseminated nature of the available low quality ores, which require fine grinding to liberate the mineral values in the ore. A large part of conventional technology is inadequate for the processing of particles of such fine size. Besides the problem of beneficiation of low quality ores, two other factors, which make it necessary to develop adequate technology, are the increasing loss of values during processing and the environmental problems associated with the disposal of fines wastes. The amount of values lost as fines, due to the inefficiency of current processes to treat fine sized ores, constitute a large fraction of the total mined values. For example in the U.S (1) alone about one-third of the phosphate mined in Florida, a large extent of the copper and one-tenth of the total iron are lost as fines. One fifth of the world tungsten mined and one-half of the tin mined in Bolivia are reported to be lost in the same manner. Serious disposal problems, on the other hand, result from the presence of fine particles in the form of an aqueous slurry.

"Fines" is a term used in particulate technology to

refer to specific size fractions. In coal processing, for example, fines are the -28 mesh (ϕ<595 microns) size fraction, while in another field of mineral processing, such as froth flotation, the term may cover ϕ<74 microns or sometimes smaller than 10 microns only (2,3).

The term slime is also used to mean fines or ultrafines not easily treated in mineral processing; they occur as a result of the inefficiency of the comminution process or due to the natural fine liberation size of the mineral in the orebody. The various aspects of the slime problem has been reviewed by Collins and Read (2). These factors have led to some efforts for developing the necessary technology for processing of fine particles.

One of the beneficiation approaches that has looked promising is selective flocculation. Ideally this should involve aggregation of desired mineral species into flocs leaving the other particulate species in suspension.

The main objective of the present investigation was the synthesis and characterization of a sulfide-selective flocculant.

1.1 AIM OF THIS STUDY

The purpose of this research project was to investigate the feasibility of developing a selective reagent for the selective flocculation of sulfide minerals.

The selectivity of a flocculant is largely determined by the interaction between the atoms at the mineral surface and certain functional groups of the flocculant molecule. This physico-chemical aspect has not been thoroughly studied with reference to various mineral systems. Even today the choice of flocculants for the flocculation of any particular mineral is governed largely by practical experience rather than by physico-chemical knowledge of the system. Development of new flocculants in order to achieve better selectivity should, however, be greatly aided by physico-chemical knowledge of individual systems.

It is well known that the xanthates are used as collectors for the selective flotation of sulfides. Therefore, if xanthate groups could be incorporated into the structure of a long-chain polymer such as polyvinyl alcohol, selective polyvinyl xanthate (PVX) flocculant for sulfides minerals might thus be obtained.

1.2 THE SELECTIVE FLOCCULATION PROCESS IN MINERAL SEPARATION

Standard physical separations are made in mineral

processing plants utilizing differences in the physico-chemical properties of valuable mineral and gangue minerals. Obviously, the chemical nature of the mineral may directly determine or affect the physical properties being utilized. These separation process are limited by the average size of the ground minerals particles. The upper size limit is essentially governed by the dominance of gravitational forces, which begin to interfere with the separation process at coarse sizes. The lower size limit, however, is determined by the principles of separation on which the process under consideration operates. For example, down to particle size of 20 microns, the froth flotation process achieves such separations quite efficiently in the case of sulfides, but the presence of finer particles leads to progressive deterioration of the process efficiency measured in terms of grade. In addition, the presence of ultrafine particles is also pernicious in flotation, because they usually adhere to the coarser ones (slime coating) thus spoiling the efficiency of the process. A rational interpretation of the role of particle size in flotation has been recently done by Trahar (4).

The reasons why slimes are difficult to treat are numerous and have been discussed many times elsewhere (2). Many of these difficulties, however, can be atributed to two

main characteristics which begin to dominate: The specific surface area becomes large and the mass of the particle becomes very low. When surface and interfacial properties of these particles dominate their behavior, the separation therefore ought to be based on difference in surface and interfacial properties of the materials to be separated. Aggregation of the particles from a dispersed system may be promoted by different mechanisms by means of altering the dispersion medium or by modifying the surface physico-chemical properties of the dispersed phase. Hence, destabilization of a stabilized aqueous dispersion leading to aggregation of particles can occur by any of the following mechanisms:

PHYSICAL MECHANISMS

1. Mechanical Aggregation.
2. Magnetic Aggregation.
3. Oil Agglomeration.
4. Electrostatic Charge Aggregation.

CHEMICAL MECHANISMS

1. Aggregation by Surfactants.
2. Flocculation by Polymers.
3. Aggregation using inorganic ions.

1.2.1 FLOCCULATION BY POLYMERS

TERMINOLOGY: It is desirable to make a distinction between the different terms that define the destabilisation of dispersed particles because confusion is common with respect to the following terms:

COAGULATION: To describe the compression or reduction of the electrical double layer thus resulting in particle aggregation.

FLOCCULATION: To describe aggregation by means of polymer bridging, patch model and network model mechanisms.

AGGREGATION: To describe destabilisation of dispersion by hydrolyzing electrolytes such as ferric or aluminum sulphate. This process can be considered composite in that the polyvalent ions destabilise the dispersion and the precipitated hydroxides provide bonding. Alternatively, surfactants may absorb at the solid/liquid interface rendering the solid hydrophobic, thus favouring particle-particle adhesion and destabilisation by the attraction between the hydrophobic coatings on the particles and also by the reduction in the area of the hydrophobic solid/water interface.

There has been an increasing interest in the flocculation of dispersions by polymers in the last two

decades (5). This interest arises from the many technological processes which make use of polymeric reagents. Their main use is to facilitate the separation of colloidal suspended solids from the liquid phase. Water treatment, disposal of industrial effluents and mineral processing are processes that currently utilize flocculation by polymers for solid/liquid separations either for water purification, recycling of water to the plant, cleaning aqueous effluents before disposal to a water-course, or recovery of solids.

The reason for the use of polymeric flocculants instead of inorganic coagulants in solid-liquid separation is that the process of flocculation is far more effective than ionic coagulation in giving stronger, faster settling, flocs and more permeable filter-cakes in filtration practice.

The water-soluble polymers used as flocculants include natural products such as starch, proteins, gum, guar etc., derivatives of natural products (dextrin, sodium alginate, etc.) and synthetic polymers, such as non-ionic polymers (polyethylene oxide, polyvinyl alcohol, etc.) and polyelectrolytes which are also polymeric substances (e.g: ionic polyacrylamides, polyethyleneimine, etc.).

1.2.2 PREVIOUS WORK

In principle, the selective flocculation process has been known for many years and it has been found empirically by several authors that various polymeric flocculants exhibit some degree of specificity when applied to mixed dispersed systems (6,7). A number of successful applications for selective flocculation have been demonstrated in the laboratory and pilot plant but with only a few commercial applications. At the present, there are only two known commercial applications for selective flocculation in North America. However, it is anticipated that several other commercial applications might be operating in the near future.

From 1962 to 1972, the U.S. Bureau of Mines and the Cleveland-Cliffts Iron Co. undertook a cooperative research effort to apply the principles of selective flocculation-desliming-flotation to the Tilden ore body, which previously had not responded to mineral beneficiation processes. The minerals in the Tilden ore body, located in the Marquete Iron Range, are predominantly hematite and silica with minor amounts of magnetite, and these precluded the use of low-intensity magnetic separation. Autogenous grinding, selective flocculation, and cationic flotation were the keys to making the long-known Tilden deposit a

commercial reality (8). Grinding to aproximately 85 per cent minus 25 micrometers or 500 mesh was required for mineral liberation and the production of high-grade concentrates. The selective flocculation stage was required to avoid excessive loss of the iron oxides (which in conventional desliming would report to the slime fraction) and to eliminate slime interference with cationic flotation.

The Tilden mine is the first commercial application of the selective-desliming-cationic flotation process and went on stream in the fall of 1954. Slightly more than 10 million tons of crude ore per year is mined to produce 4 millon tons of pellets. The crude ore contains 36 percent iron and can be beneficiated to 65 percent iron.

Banks (9), described the development of the second commercial application of a selective flocculation-flotation process, on a sylvinite (potash) ore at Cominco Limited's operations in Saskatchewan, Canada. The ore contained sylvite as the chief source for potash, mixed with gangue minerals such as dolomite, hematite, quartz, kaolinite, illite, chlorite and anhydrite. The gangue minerals amounted to 4.5 to 8 percent by weight of the total ore. Using the selective flocculation-flotation process, 86 percent of commercial grade potash concentrate could be recovered. The reagents used consisted of a non-ionic

polyacrylamide flocculant at 0.03 lb/ton of feed and a cationic collector, Aero 870 (American Cyanamid Co.), and ethoxylated alkylamic alkylguanidine complex at 0.04 lb/ton of feed.

A review of a number of separations by selective flocculation process and the feasibility of its use on binary, ternary and multi-mineral systems has been presented by Read and Hollick (10). Most of the work has been concerned with the treatment of clays, iron minerals, phosphates and potash.

The best concentration ratios have been obtained from laboratory trials only at optimun conditions of low solid content, high feed grade and high specific gravity of the component to be flocculated, etc. For example, Yarar and Kitchener (11) have successfully separated galena from a synthetic mixture with quartz.

Read (12) at Warren Spring Laboratory, England, has conducted a series of studies on the selective flocculation either of hematite or a silicate from mixture by varing the anionic character of the partially hydrolyzed, polyacrylamide flocculant employed. Different separation methods have been developed for hard and soft water media. Electrokinetic and infrared techniques have been employed in the elucidation of the mechanism whereby selectivity has

been attained in the different cases. Thus, synthetic mixtures of hematite and siliceous gangue slimes, with a particle size less than 20 microns, were successfully separated by selective flocculation.

Lien et al.(13) described Algoma's efforts to concentrate their iron ores by the selective flocculation process. The iron ore contained hematite and magnetite as the main iron minerals, with hematite being the predominant one, all amounting to about 30 percent iron. The particle size of hematite ranged between 5 to 30 microns, while that of magnetite was from 20 to 200 microns. The main gangue minerals were quartz, carbonate and chlorite. The process was applied successfully in the laboratory and pilot plant using two stages of grinding and a total of four selective flocculation-steps. Corn starch was used as the selective flocculant, and sodium silicate was employed as a dispersant.

Attia and Kitchener (14) prepared and tested a number of water-soluble polymers of high molecular weight, incorporating sulphdryl (-SH) or other groups which complex or chelate heavy metals ions. Evidence for selectivity of flocculation with synthetic mixtures of finely-divided minerals has been obtained.

Attia (15) also reported in more detail the preparation

and characterization of the PAMG selective flocculant for copper minerals. The reactions were confirmed by various techniques, but the exact structure could not be confirmed. Fractionation of PAMG by membrane filtration and gel chromatography was reported. The PAMG produced good flocculation on suspension of chrysocolla.

Dispersion flocculation and selective flocculation studies were perfomed on mixtures of chrysocolla and quartz by Rubio and Goldfarb (16). Anionic, cationic, and non-ionic polyacrylamide flocculants were compared in this investigation.

Rubio and Kitchener (17) achieved selective flocculation of copper minerals from simulated and natural ores by first treating the dispersed minerals with a conventional flotation collector, which is selective to copper minerals, to induce hydrophobicity on their surfaces. Then, by the addition of a partially hydrophobic flocculant, such as polyethylene oxide, the hydrophobized copper minerals (mainly malachite and chrysocolla) could be flocculated, leaving the hydrophillic gangue minerals (mainly quartz and clays) in suspension.

Clauss et al. (18) have modified polyacrylamide to give a linear polymer containing 69 percent amide, 23 percent carboxylic and 8 percent hydroxamic acid groups. The

modified polymer selectively flocculated cassiterite from mixtures with quartz.

Applications of selective flocculation to clay involve either the separation of quartz from clays, or the separation of opaque, coloring minerals, such as rutile and hematite from kaolin clays to obtain superior optical properties.

Mercade (19) patented a selective flocculation process for the removal of quartz from kaolin clay. Kaolin clay contaminated with quartz was purified by dispersing it in water to form a suspension. A soluble compound containing polyvalent cations and an organic weakly anionic polyelectrolyte flocculant were added, and the suspension was stirred until flocs of quartz formed and settled out.

Maynard (20) also achieved the removal of rutile (TiO_2) and hematite (Fe_2O_3) from Georgia clay by the selective flocculation of rutile with a hydrolyzed polyacrylamide. Thus improving the whiteness of clay.

Selective flocculation of kaolin from rutile and hematite was also achieved by Sheridan (21), who described a process to that effect. The process consisted of deflocculating an aqueous suspension of the impure clay by adding an alkali metal silicate. The clay particles were then selectively flocculated by adding a synthetic organic

polyanionic flocculating agent, such as weakly anionic, partially hydrolyzed, polyacrylamide. A concentrate of deflocculated impurities was then separated. An improvement of clay purity and brightness was realized.

Selective flocculation of bauxite from iron-bearing minerals and other clays was investigated by Lifirenko and Volova (22) who have shown that selective flocculation made it possible to remove the bulk of the most finely dispersed material (minus 0.5 microns) containing high concentration of Fe_2O_3, from the bauxite flocs, while at the same time thickening the bauxite product to 45 percent.

An investigation was made by Christodoulou (23) on a red mud composed of 30.1 percent Fe_2O_3, 9.3 percent Al_2O_3, 8.1 percent SiO_2 and 6.6 percent TiO_2. The results of flocculation tests at pH 9, 10, and 11, indicated the possibility of separating hematite and rutile from red mud suspensions.

There has not been much progress in applying selective flocculation technology to recover the phosphate fines which are still lost as wastes since Haseman (24) patented his method for selectively flocculating phosphate fines, particles from associated clays.

Davenport (25) also tested the feasibility of

recovering phosphate from minus 20 micron fines following Haseman's procedure and concluded that is was technically feasible to beneficiate hard-rock phosphate slimes by selective flocculation; however, he also concluded that the high cost of dewatering the concentrate would impose a serious economic handicap. Pradip et al. (26) have investigated the adsorption of polyacrylamide on apatites. The slightly anionic polyacrylamide used (Separan NP 10) was found to be an excellent flocculant for both hydroxy-and fluor-apatite. It was concluded in this study that the flocculant adsorption and flocculation of the apatite were enhanced as the suspension pH becomes acidic.

Yarar and Ozgur (27) studied the feasibility of the separation of SiO_2 and $MgCO_3$, by selective coagulation and flocculation from an artificial mixture or natural ores containing $MgCO_3$ and SiO_2. A number of commercial polymeric flocculants of anionic, cationic, and non-ionic character were investigated. It was found that any of the anionic flocculants could selectivily flocculate $MgCO_3$, keeping - quartz in suspension.

Carta et al. (28) reported their investigation on recovering ultrafine fluorite from natural ores by selective flocculation. The ore was characterized by an extremely fine size distribution, and contained barite, fluorapatite,

calcite and clays in addition to fluorite. The ore was first subjected to flotation, however, to recover the relatively coarse barite minerals. The finely ground fraction was then subjected to a two-stage selective flocculation separation. The first step was to selectively flocculate the barite at pH 8.2, using ammonium alginate (2kg/ton) and sodium silicate (100mg/l), leaving the fluorite in suspension. The second step was to selectively flocculate fluorite at pH 6.2, also with ammonium alginate as the flocculant.

Attia (29), has recently summarized the main applications of selective flocculation.

1.2.3 SELECTIVE FLOCCULATION BY POLYMER

The principles governing a practical selective flocculation process were summarized as nine rules by Yarar and Kitchener, listed in appendix 1. The fundamental premise in such operations is the selective uptake of the added polymer, by the solid component(s) meant to be flocculated, thus faciliting separation as represented schematically in Figure 1. Selective polymer uptake by suspended solid is governed by sets of variables relating to (i) suspended solids, (ii) conditions prevailing in the solution, (iii) properties of the polymers themselves, and

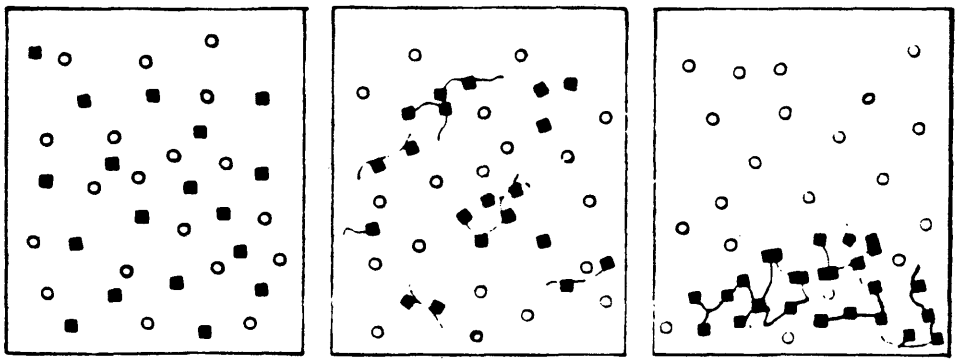


Figure 1. Idealized process of selective flocculation in a two component system. (a) suspension of two minerals, (b) added polymer taken up by one component, (c) flocculated component sedimenting selectively after B. Yarar (3)

energetic, kinetic as well as hydrodynamic conditions of the overall system as represented in Figures 2 and 3.

1.2.4 THE BRIDGING MECHANISM OF FLOCCULATION

The general picture accepted under the title "bridging" is that the gap between suspended particles is bridged by a polymeric string, as it were, in effect increasing the sizes of colloidal entities (3). Preferential adsorption of a flocculant on a mineral particle and subsequent flocculation by interparticle bridging are dependent on the interfacial potential at the particle surface, fraction of the particle surface covered by the flocculant, and the chemical nature of both the particles and the flocculant. Chemical principles governing adsorption of polymeric flocculants on particles are, to a large extent, similar to the adsorption of collectors in conventional flotation process.

1.2.5 THE PATCH MODEL AND NETWORK MODEL

It is noted that polymeric flocculant molecules can act as charge-neutralizing units, if their active groups are of opposite sign to that of the net charge sign of the particle, while simultaneously acting as bridging agents (3).

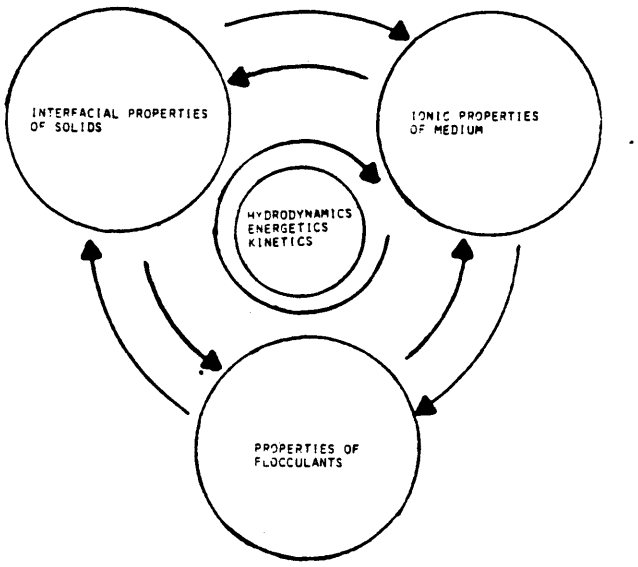


Figure 2. The complex inter-relation of factors prevailing in a flocculation system.

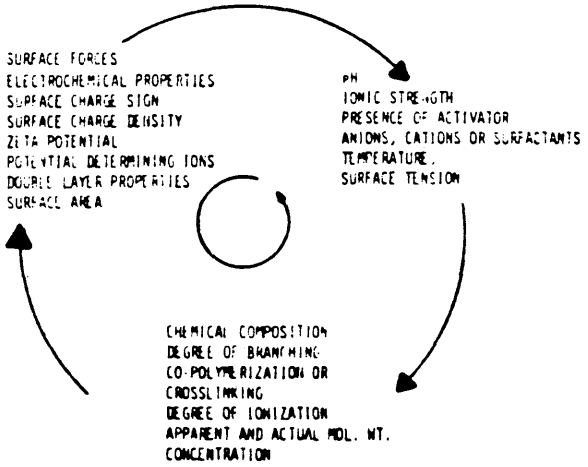


Figure 3. Variables determining the properties of a flocculation system and their inter-dependence (to be viewed together with Figure 2. [after B. Yarar (3)]

A less commonly recognized flocculant ion model has been put forward by Vanderhoff where the polymer solution is assumed to form "a network" through hydrogen bonding, interchain cross links by multivalent ions, London-van der Waals bonds and other types. Although a number of arguments of this hypothesis have been put forward by the author, its compatibility with selective flocculation phenomena has been questioned by Yarar (3).

1.2.6 MECHANISM OF FLOCCULANT ADSORPTION

Numerous mechanisms of polymer adsorption have been suggested by authors for various systems. These mechanism can be summarized as follow:

i) Hydrogen Bonding occurs when hydrogen is attached to an electro-negative element, such as F, N, S, O. The interaction of freshly ground natural silica or clays with non-ionic polyacrylamides has been accepted to be by this mechanism (30).

ii) Electrostatic Interaction takes place if the functional groups of the polymer and the solid are oppositely charged. The attraction is non-specific and results in mutual charge neutralization and even charge reversal. The flocculating action of cationic flocculants on negatively charged solids is usually of this nature.

iii) Chemical Interactions are observed when flocculants and suspended solids have groups capable of specific interactions, forming salt-like structures or complexes. The interaction of modified starch with calcium phosphate (30) has been suggested to be due to calcium salt formation. The blocking of Ca^{+2} sites on $CaSO_4$ by the $-COO^-$ groups of polyacrylamide has also been reported (31).

iv) The flocculating action of a non-ionic polymer on CaF_2 (fluorite mineral) has been atributed to the possible interaction of the dipoles of the amide group with the electrostatic field of the surface of the ionic crystal (32). A similar suggestion was made by Steiner to account for the adsorption of tannins on fluorite.

v) Hydrogen Bonding has been employed as a means of non-ionic polymer uptake by fines of which the surface properties were initially modified by a non-polymeric surfactants (17). The mechanism of bond formation appears to be related to that of shear flocculation, where, London-van der Waals forces are evidently the major cause of attraction.

It is evident from the discussion above that, depending on the nature of the interaction energy involved between the solid and the active group of the polymer, the nature of the

chemical bond involved in the adsorption process can be expected to vary. In all cases, however, it is possible that polymers require a large number of points of attachement for strong adsorption. The actual number is not presently known with certainity for ordinary polymers.

1.2.7 SELECTIVE ADSORPTION AND FLOCCULATION

Selective adsorption of polymer molecules can be achieved by i) adjusting the chemical composition of the suspending medium (determines the interfacial potential) in order to exploit the dependence of adsorption of ionic polymers on the interfacial potential at the particle/water interface, ii) introducing into the polymer active groups that will form complexes or salts with the metal species on the surface of the desired mineral, and iii) the use of reagents (usually, depressants as in froth flotation) such as sodium silicate and sodium sulfide which would absorb on relevant mineral surfaces and thereby prevent adsorption of polymers, or of activators which induce adsorption of polymers on desired minerals.

1.2.8 ROLE OF FUNCTIONAL GROUPS

It is well known that adsorption of froth flotation collectors and modifiers on particles depends on active

groups present in the collector or modifier molecules. The following are some examples of active groups:

1. Carboxylate, as in fatty acid collectors.
2. Sulfonate, as in petroleum acid collectors.
3. Mercaptan or thiol group, as in xanthate collectors.
4. Hydroxyl, in depressors such as starches and tannins.
5. Cyanide, in depressing certain sulfides during flotation by xanthates.

The chemical features of polymers are in several ways similar to those of flotation collectors. Thus in the past, selectivity has been obtained by incorporating some of these active group into the polymeric chain (33-37).

Attia and Kitchener (14) have reported selective flocculation of oxidized copper ore using cellulose modified to contain xanthate. Clauss et al. (18) have also reported the separation of cassiterite from its mixtures with quartz using modified polyacrylamide, containing hydroxamic groups.

1.3 POLYVINYL XANTHATE

The literature concerning the synthesis of polyvinyl xanthate is rare. In 1952, a Japanese researcher (38) published a paper regarding the xanthation of polyvinyl alcohol (PVA); information concerning the preparation of

xanthate and on the composition of the formed product is not given. In 1957, Nicco (39) in France, described possible xanthates of polyvinyl alcohol. Iodometry was used as the method of quantifying xanthate.

1.4 GENERAL APPROACH

The major contribution to fine particles separation expected from this work would be derived from results on the synthesis of a sulfide selective-flocculant.

The flocculant synthetized would be called polyvinyl xanthate-2000 (referred troughout thesis as PVX-2000), polyvinyl alcohol of average molecular weight 2000 was used in the synthesis in this investigation.

The work was conducted in three separate phases: 1) synthesis, 2) characterization, 3) flocculation testing.

1. SYNTHESIS

The synthesis involved the preparation of PVX-2000. This product is the result of the reaction of polyvinyl alcohol with potassium hydroxide and carbon disulfide.

The crude product of the synthesis of PVX-2000 also contains products of side reactions between potassium hydroxide and carbon disulfide. The purification of the crude PVX-2000 was effected by precipitating it with

different organic liquids such as acetone, methanol, ethanol and carbon tetraclhoride, as is done in the purification of commercial xanthate.

2. CHARACTERIZATION

Ultra-violet and Infrared spectroscopy techniques were used to identify the reaction products.

It is well known (see 1.7.1) that the adsorption of radiation in the ultra-violet region by xanthate allows the determination of xanthate in solution. Similarly, the comparison between the ultra-violet spectrum of the crude product reaction and purified product could reveal whether the purification has been achieved.

The infrared spectrum of PVA and the synthesized PVX-2000 could indicate the change in PVA spectra and identify C=S and C-O vibrations, which are characteristic of xanthate. If xanthate has been attached to the PVA backbone, the C=S and C-O vibration should appear in the infrared spectra of the synthesized PVX-2000.

In order to quantify xanthate attached to PVA, iodometry and ultra-violet spectroscopy seem to be the most promising methods.

3. FLOCCULATION

Flocculation of single sulfide minerals (pyrite, chalcopyrite, galena) and quartz is studied using synthesized PVX-2000 as a function of suspension pH and polymer dosage. The idea is to identify conditions for selective flocculation of a single mineral from its mixture with other mineral.

With the result obtained in single mineral flocculation by PVX-2000 with pyrite, chalcopyrite, galena and quartz, separation tests on synthetic mixtures of pyrite/quartz, galena/chalcopyrite, and galena/pyrite were conducted. These series of tests provided information regarding the selectivity of PVX-2000 towards sulfide minerals.

1.5 POLYVINYL ALCOHOL

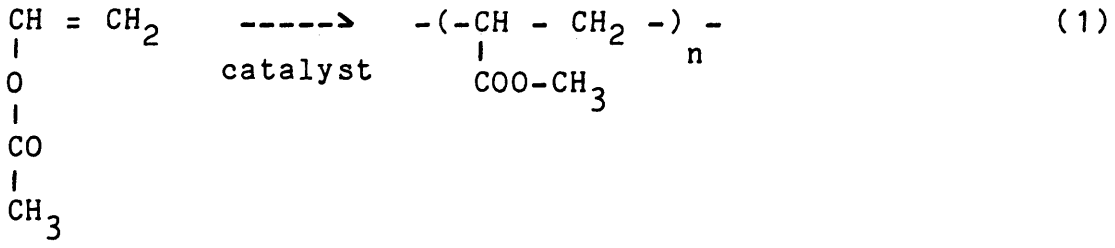
Polyvinyl Alcohol (PVA) was first synthesized in Germany by Herman and Hachnel (40) in 1924.

All PVA manufacture involves polyvinyl acetate as the starting material. The theoretical monomer, vynyl alcohol (CH_2=CHOH), does not exist except as an insignificantly small component of samples of its keto tautomer, acetaldehyde (CH_3-CHO). Although other polyvinyl esters can be used as starting materials, economics favors

the use of polyvinyl acetate. Conversion of polyvinyl acetate to PVA is generally accomplished by base-catalyzed methanolysis; sodium hydroxide is the usual base (see appendix 2).

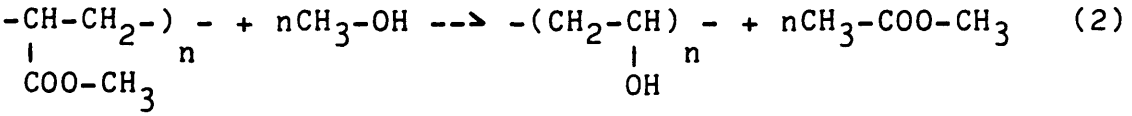
The alcoholysis reaction can also be catalyzed with a strong acid, eg. sulfuric or hydrochloric. However, this process is not practiced industrially because of the relatively slow reaction rate and severe corrosion problems.

Polymerization of vinyl acetate and conversion of the polymer to PVA are illustrated below.



(1)

Vinyl Acetate Polyvinyl Acetate



(2)

Polyvinyl Acetate	Methanol	Polyvinyl Alcohol	Methyl Acetate

Polyvinyl acetate polymerization is accomplished by conventional process, eg., solution bulk, or emulsion polymerization. Solution polymerization is favored because the subsequent alcoholysis reaction requires solvent addition. The polymerization step controls the ultimate molecular weight of the PVA. Catalyst selection, temperature, and solvent control the degree of polymerization; acetaldehyde is an effective chain-transfer agent, as are agents commonly used in polymerization of vinyl monomers.

The degree of hydrolysis of PVA is controlled during the alcoholysis reaction and is independent of molecular-weight control. Fully hydrolyzed PVA is obtained if methanolysis is allowed to go to completion. The reaction can be terminated by neutralizing or removing the sodium hydroxide catalyst. The addition of small amounts of water to the reactants promotes saponification of polyvinyl acetate, which consumes sodium hydroxide. The extend of hydrolysis is inversely proportional to the amount of water added. A disadvantage of water addition is an increase in by-product sodium acetate, which is present as ash in all commercially available grades of PVA. The alcoholysis reaction can be carried out in a highly agitated

slurry process; a fine precipitate forms as the polyvinyl acetate converts into PVA. The product is then washed with methanol and is filtered and dried. A moving-belt process allows the PVA to form a gel and subsequently to be cut into granular form.

The alcoholysis process yields methyl acetate as a by-product. The methyl acetate can be used as a solvent or it can be processed to recover methanol and acetic acid. Table 1 shows the physical properties of PVA.

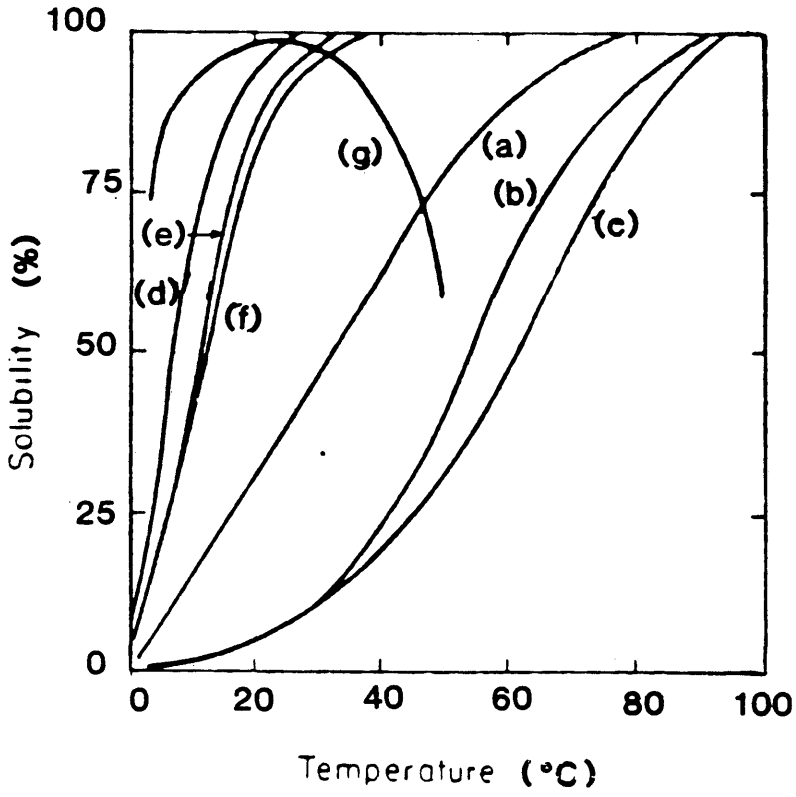
1.5.1 SOLUBILITY IN WATER

PVA is used mainly in aqueous solution. Its solubility in water depends on its degree of polymerization and degree of hydrolysis. Since the presence of the residual hydroxyl group weakens hydrogen bonding between the intra-and intermolecular hydroxyl groups, the solubility of partly hydrolyzed PVA in water is higher than that of fully hydrolyzed PVA.

Figure 4, shows the solubilities of typical commercial grades of PVA, with a degree of polymerization between 500 and 2400, and which are 81-98 percent hydrolyzed depending upon the temperature.

Table 1. Physical Properties of Polyvinyl Alcohol

Property	Value
Appearance	White to cream granular powder
Specific gravity: of solid of 10 wt %sol.	 1.27-1.31 1.02 at 20°C
Thermal stability	Gradual discoloration above 100°C; darkens rapidly above 150°C; rapid descomposition above 200°C
Refractive index (film)	1.55 at 20°C
Thermal conductivity	1.39 Btu-in./h-ft^2·°F
Electrical resistivity	(3.1-3.3) X 10^7 ohm-cm
Melting point (unplasticized)	230°C for fully hydrolyzed grades; 180-190°C for partially hydrolyzed grades
Storage stability (solid)	Indefinite when protected from moisture
Flammability	Burns similarly to paper
Stability in sunlight	Excellent



	Hydrolysis (mol%)	Degree of Polymerization
(a)	98-99	500-600
(b)	98-99	1700-1800
(c)	98-99	2400-2500
(d)	87-89	500-600
(e)	87-89	1700-1800
(f)	87-89	2400-2500
(g)	78-81	2000-2100

Figure 4. Water solubility against solution temperature for polyvinyl alcohol (40)

1.6 XANTHATE

Xanthates are salts of xanthic acid, which is essentially alkyl dithiocarbonic acid with two oxygen atoms in carbonic acid replaced by sulfur and one hydrogen atom replaced by an alkyl group.

Xanthates were discoverd by Zise in 1822. The introduction of xanthates as mineral collectors in the 1920s provided a strong impetus to the detailed study of these compounds. Methods of preparation, purification, and analysis were standardized for the fundamental studies.

Xanthates are the reaction products of carbon disulfide, an alcohol, and an alkali. They are formed by combination of the three reactants in the stoichiometric ratio 1:1:1, with the elimination of water.

The general reaction is:

$$ROH + MOH + CS_2 \longrightarrow ROC(=S)-SM + H_2O \qquad (3)$$

where R stands for an alkyl hydrocarbon and M denotes a monovalent metal such as sodium or potassium. The details of preparing potassium ethyl xanthate were first described by Foster (41) and Keskyula (42).

1.6.1 XANTHATE IN MINERAL FLOTATION

Flotation is undoubtedly the most important and versatile mineral processing technique. Originally patented in 1906, flotation has permitted the mining of low grade and complex ore bodies which would have otherwise been regarded as uneconomic.

Flotation is a selective process and can be used to achieve specific separations from complex ores such as lead-zinc, copper-zinc, etc. Initially developed to treat the sulfides of copper, lead and zinc, the field of flotation has now expanded to include the oxidized minerals and non-metallics, including fine coal.

The theory of froth flotation is complex and is not completely understood (43).

Froth flotation utilises the differences in physico-chemical surface properties of particles of various minerals. After treatment with reagents, such differences in surface properties between the minerals within the flotation pulp become apparent and, for flotation to take place, an air bubble must be able to attach itself to a particle, and lift it to the surface of the water.

In flotation concentration, the mineral is usually transferred to the froth or float fraction, leaving the gangue in the pulp or tailing. This is direct flotation as

opposed to reverse flotation, in which the gangue is separated into the float fraction.

The air bubbles can only adhere to the mineral particles if they can displace water from the mineral surface, which happens if the mineral is to some extent water repellent or hydrophobic. To achieve these conditions it is necessary to use chemical reagent known as collectors, which adsorb on mineral surfaces, rendering them hydrophobic thus facilitating bubble attachment. The most widely used collectors are of the sulphydryl type, where the polar group contains bivalent sulfur. They are very powerful and selective in the flotation of sulfide minerals. The most widely used of these anionic collectors are the xanthates and dithiophosphates. The xanthates are the most important for sulfide mineral flotation.

1.7 SPECTROPHOTOMETRIC METHODS

1.7.1 UV-SPECTROSCOPY

The absorption of radiation in the ultraviolet region by xanthate allows its determination in solution. Bushell and Malnarich (46) first obtained the spectrum of potassium isopropyl xanthate in the region 200-350 nm. As shown in Figure 5, xanthate shows two absorption maxima, the one at 301 nm being the more intense.

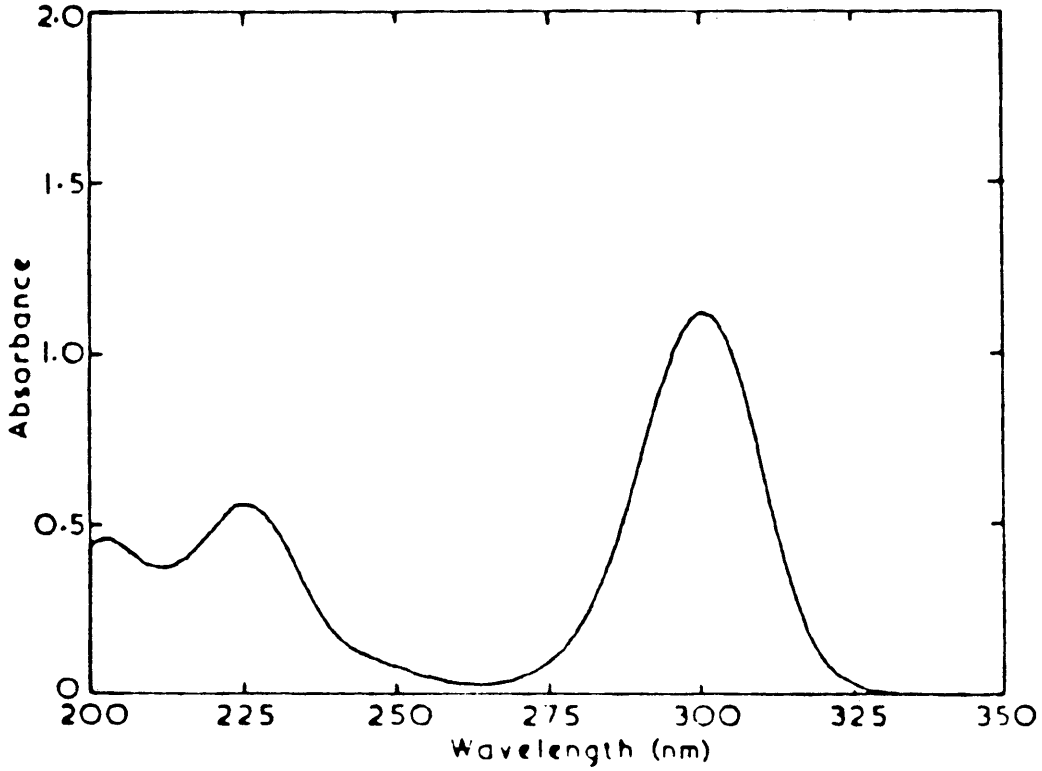


Figure 5. UV absorption spectrum of 10.0 ppm solution of potassium ethyl xanthate in 1-cm cell with linear wavelength and absorbance presentation (after H. Jones & J.T. Woodcock: Inst. Min. Metall. 1973)

Intensity of absorption of light of this wavelength (301 nm) follows the Beer's law relationship between concentration and absorbance and can be used for the spectrophotometric determination of xanthate. The concentration range that falls within the Beer's law plot has been shown to be 0-25 mg/l. The method is useful in xanthate analysis in flotation plants, for automatic reagent regulation systems and in research laboratories.

1.7.2 INFRARED SPECTRA OF XANTHATES

Little et al. (47) obtained the spectra of alkaline metal xanthates with different hydrocarbon chains, and assigned the xanthate vibrational frequencies. The absorption bands in the region 1000-1200 cm^{-1} in the spectra of alkali metal xanthates are not well resolved, but it is possible to distinguish three reasonably distinct groups of bands corresponding to 1200, 1130, 1060 cm^{-1} for the heavy metal xanthates.

A detailed analysis of the infrared spectra has been described by Shankaranarayana and Patel (48). They assigned values for the charateristic frequencies of C=S and C-O groups and compared them for various xanthate compounds. These values are listed in Table 2.

The assignment of the C=S frequency around 1200 cm^{-1}

Table 2. Characteristic Frequencies of C=S and C-O Groups of the Derivatives of Xanthic Acid.[a]

Substance	Medium	C=S Frequency, cm^{-1}	C-O Frequency, cm^{-1}
Sodium ethyl xanthate	Nujol mull	1179	1040
Potassium ethyl xanthate	KBr disk	1143	1055
Potassium n-butyl xanthate	Nujol mull	1153	1077
Cuprous ethyl xanthate	Nujol mull	1200	1037
Zinc ethyl xanthate	Nujol mull	1212	1035
Lead ethyl xanthate	Nujol mull	1220	1020

[a] Table taken from reference (48).

and the C-O frequency around 1030 cm^{-1}, as indicated in the studies of Shankaranarayana and Patel (48), differs sligthty from the values assigned by Litle et al. (47). For the purpose of this research the values given by Shankaranarayana and Patel will be used to identify the C=S and C-O frequency in the synthesized PVX-2000 spectra.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The investigation was conducted in three separate phases:

1. Synthesis
2. Characterization
3. Flocculation Tests

2.1 SYNTHESIS

Polyvinyl xanthate-2000 (PVX-2000) was prepared by the reaction of polyvinyl alcohol, and alkali and carbon disulfide. Polyvinyl alcohol (PVA) used was 75 % hydrolyzed and had an average molecular weight of 2000.

The PVA, potassium hydroxide and carbon disulfide were combined in stoichiometric proportions. First the PVA was dissolved in distilled water over a stirrer hot plate. The temperature of the solution was kept about the boiling point. Potassium hydroxide had been prepared as an aqueous solution.

PVA solution and aqueous potassium hydroxide were mixed in an Erlenmeyer flask over a stirrer hot plate, the temperature was kept at 80 ^{o}C, and the mixture stirred for about 2 hours. The color of the mixture gradually changed from white to yellow; this mixture was called alcoholate solution. The alcoholate was cooled to room

Table 3.

Chemical Reagents used and their specifications

Polyvinyl Alcohol - 75% hydrolyzed, average molecular weight 2000, Aldrich Chemical Company.

Potassium Hydroxide - 85.5% KOH, pellet, J.T. Baker Chemical Co.

Carbon disulfide - A.C.S. Fisher Scientific Co.

Methyl alcohol - 99.9% CH_3-OH, Fisher Scientific Co.

Acetone - 99.5% CH_3-CO-CH_3; Fisher Scientific Co.

Hydrochloric acid - 36.5 - 38% HCl, Fisher Scientific Co.

Spectro-check reagent kit - Manufactured by LANCER Division of Sherwood Medical.

temperature. Then, a stoichiometric quantity of carbon disulfide was added, and the mixture stirred for four hours. Under these conditions the mixture took on a reddish orange color.

The reddish orange colored solution was unpurified PVX-2000, which contained the products of side reactions between the potassium hydroxide and carbon disulfide, mainly thiocarbonates.

2.1.1 PURIFICATION OF PVX-2000

PVX-2000 is unstable in aqueous solution, as indicated by the evolution of hydrogen sulfide. The hydrogen sulfide was detected due to its unpleasant odor and also with the lead acetate paper test. When the lead acetate paper was put over the mouth of the beaker which contained the PVX-2000, the escape of hydrogen sulfide blackened the paper. The purification of PVX-2000 was achieved by precipitating the PVX-2000 and leaving other products in solution. This method is known as "fractionation of high polymer". In a general sense the fractionation of a macromelecular substance consists of the separation of that substance into its different molecular weight fractions. This technique consists of:

- Addition of non-solvent. Succesive precipitation of

polymer species from a solution by addition of a miscible non-solvent, where the larger molecules precipitate first. - Lowering the temperature. Succesive precipitation of polymer species from a solution by controlled cooling.

2.1.2 PROCEDURE

Tests of the precipitation of PVX-2000 by an organic solvent such as methyl alcohol, ethyl alcohol, carbon tetrachloride or acetone were conducted. The tests were also conducted using mixtures of the above organic solvents.

A mixture of acetone-methanol (50-50%) was found to be the optimun non-solvent. This mixture was added drop by drop from a burete to 25 ml of PVX-2000 contained in a 250 ml Erlenmeyer flask until the solution became turbid. During the addition of the acetone-methanol the solution of PVX-2000 was kept magnetically agitated.

As soon as the solution became turbid the Erlenmeyer flask was transferred to a shaker machine and kept agitated overnight. The formation of a yellow pale precipitate was observed. In order to maximize the precipitation of polymer, the Erlemmeyer flask containing the solution and precipitate (the product forming overnight) was transferred to a water-bath, where the temperature was decreased from room temperature to 5 ^{o}C. Then the precipitate formed

was vacuum-filtered and dried in a vacuum dryer overnight.

2.1.3 DEGREE OF XANTHATION

Noting that xanthate attachement on the PVA backbone may depend on the potassiun hydroxide and carbon disulfide concentration, several tests were conducted in which the concentration of either potassium hydroxide or carbon disulfide was in excess of the stoichiometric amount required. It is also a known practice in commercial xanthate production to add caustic soda in order to slow down the decomposition of xanthate. Some tests were conducted applying this fact, in order to check whether it increased the degree of xanthation. The xanthate attached to the backbone of PVA was quantitatively determined and the results are discussed in section 3.3.

2.2 CHARACTERIZATION

PVX-2000 was characterized using ultra-violet and infrared spectroscopy techniques.

2.2.1 ULTRA-VIOLET SPECTROSCOPY

All spectra were obtained using a Coleman, Model 46 UV-VIS Spectrophotometer. This is a single-beam, grating spectrophotometer with a spectral range from 195 to 800 nm

and a continuously variable slit width. Reading in absorbance, 0 to 2 A linear absorbance and quartz cells of 10mm were used. Wavelengths were calibrated with a Spectro-Check reagent kit. Spectra were obtained over the range 200-400 nm.

Stock solutions containing comercial ethyl xanthate and PVX-2000 were freshly made in water on the day absorbance measurements were made. The absorbance at 302 nm was used to construct the calibration line of commercial ethyl xanthate and purified PVX-2000. The spectra of unpurified and purified PVX-2000 were also obtained in the 200-400 nm region.

2.2.2 INFRA-RED SPECTROSCOPY

The infrared spectra of purified PVX-200 and PVA were obtained, using a Perking-Elmer, Model 281 spectrophotometer. Potassium bromide pellets were made with PVA and purified PVX-2000. The weight of the material and potassium bromide that gave better spectra are listed in Table 4.

TABLE 4. Composition of pellets used in the infrared spectroscopic analysis.

Compound	Wt. Material(mg)	Wt. KBr(mg)
PVA	1.5	300
PVX-2000	3.0	300

The pellets were prepared in an identical manner. First, the appropiate amount of KBr was mixed with the material sample to allow for the desired pellet composition. Then, the sample and KBr were ground in an agate mortar and pestle until a uniform consistency was achieved. The desired total amount of the pellet was then weighed out, and the pellet was compressed at 23000 psi for 7 minutes under vacuum. The spectra of PVA and PVX-2000 were obtained in the 4000-600 cm^{-1} region.

2.3 FLOCCULATION TEST

2.3.1 MATERIALS

Natural minerals used in this study (pyrite, chalcopyrite, galena, and quartz) were obtained from the Museum of Geology at the Colorado School of Mines. Samples

were obtained in the purest form available.

2.3.2 SLIME PREPARATION

Pyrite, Chalcopyrite, galena and quartz were ground and pulverized. The ground minerals were dry-screened using a 400 mesh screen and the minus 400 mesh fractions were stored in glass stoppered bottles.

2.3.3 SINGLE MINERAL FLOCCULATION

Test on single mineral flocculation were carried out in graduated 100 ml glass-stoppered cylinder. The mineral suspension was prepared at 1% solids content.

The pH was adjusted using hydrochloric acid and potassium hydroxide solutions. The suspension was agitated and required amounts of PVX-2000 added. The cylinder was inverted twenty times and then the mineral was allowed to settle under gravity for 3 minutes.

The contents of the cylinder were poured over a 3.5 inches diameter 400 mesh screen, and the plus 400 mesh fraction was taken as the flocculated fraction. The minus 400 fraction was the unflocculated material. The unflocculated material was filtered, dried and weighed. The material flocculated was calculated by weight difference and expressed as percentage of the total weight of solid.

2.3.4 SELECTIVE FLOCCULATION FROM SYNTHETIC MIXTURES

Synthetic binary mixtures of minerals were prepared by mixing equal quantities of minus 400 mesh fractions of the constituent minerals. The mixture was equilibrated by stirring for one day before further experimentation.

Selective flocculation experiments were performed in 100 ml graduated test tubes. The mineral suspension was prepared at 2% solid content. The synthetic mixture was added to the cylinder at the appropiate pH. The suspension was agitated and the required amount of PVX-2000 was added. The cylinder was inverted twenty times and the contents allowed to settle under gravity.

The contents were poured onto a 400 mesh screen. The plus 400 fraction was due to floc formation and the minus 400 fraction was unflocculated material. The flocculated and unflocculated fractions were filtered, dried and weighed. Assays of flocculated and unflocculated material were made using a Perking-Elmer, Model 306 Atomic Absorption Spectrophotometer. The recoveries of minerals were calculated for each fraction.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The results obtained during this investigation presented in three separate sections: 1) Synthesis, 2) Characterization, 3) flocculation.

3.1 SYNTHESIS OF PVX-2000

The procedure described in the experimental section was the result of many tests conducted in order to obtain the synthesis of PVX-2000. The change of color during the reaction of PVA and potassium hydroxide from colorless to yellow is in agreement with published (50,51) work in the preparation of commercial xanthate. This is due to the interaction of alcohol with alkali, and this compound was called alcoholate.

The reaction proposed is:

$$-(-CH_2-CHOH-)_n- + KOH \dashrightarrow -(-CH_2-\underset{\displaystyle OK}{CH}-)_n- + H_2O \qquad (4)$$

Potassium hydroxide was used instead of sodium hydroxide since it is known (50) that potassium hydroxide reacts energetically and more completely with alcohols than sodium hydroxide.

The next step was the reaction of the alcoholate with carbon disulfide to obtain xanthate. After the required carbon disulfide had been added slowly and kept agitated with a stir bar on a magnetic stirrer for about 6 hours, the solution changed to reddish orange color. This color results from the formation of alkali sulfides by a side reaction between potassium hydroxide and carbon disulfide.

The main reaction proposed for xanthation is:

$$-(-CH_2-CHOH-)_n- + nKOH + nCS_2 \longrightarrow -(-CH_2-\underset{\underset{O-CSSK}{|}}{CH}-)_n- + nH_2O \quad (3)$$

PVA PVX-2000

In explaining their results about the side reaction during the production of xanthate many authors (52,53,54) mention the formation of thiocarbonates.

The following are the probable secondary reactions:

$$-(CH_2-\underset{\underset{O-CSSK}{|}}{CH}-)_n- + H_2O \rightleftharpoons HOCSSK + -(-CH_2-CH-)_n- \quad (6)$$

$$HOCSSK \rightleftharpoons CS_2 + KOH \quad (7)$$

$$5CS_2 + 12KOH \rightleftharpoons K_2S + 2K_2CO_3 + 3K_2CS_3 + 6H_2O \quad (8)$$

$$CS_2 + K_2S \rightleftharpoons K_2CS_3 \quad (9)$$

$$K_2CS_3 + 3H_2O \rightleftharpoons K_2CO_3 + 3H_2O \quad (10)$$

$$K_2CS_3 + 2H_2O \rightleftharpoons H_2CS_3 + 2KOH \quad (11)$$

$$H_2CS_3 \rightleftharpoons H_2S + CS_2 \quad (12)$$

$$K_2CS_3 + 3KOH \rightleftharpoons 3KHS + NaCO_3 \quad (13)$$

The method of purification used permitted the recovery of 94% of the PVX-2000 formed. The synthesized PVX-2000 is completely soluble in cold water.

3.2 CHARACTERIZATION

3.2.1 ULTRA-VIOLET SPECTRA

The UV-spectrum obtained of unpurified PVX-2000 is shown in Fig. 6. From this spectrum it is possible to distinguish the following peaks: 212, 227, 302, and 282 nm.

Xanthate ion (55) absorbs at 301 and 226 nm in a 2:1 ratio. However, it seemed that xanthate absorption peaks were shifted slighty to 227 and 302 nm. Nevertheless, the absorption at 227 nm is almost twice that at 302. It is reported in the literature (55) that monothiocarbonate absorbs in the region 220-230 nm. The peak at 227 nm may also be attributed to monothiocarbonate ion.

It has been also reported (54,56) that the peak at 382 nm may correspond to xanthate or trithiopercarbonate ($CS_3O^=$) ion.

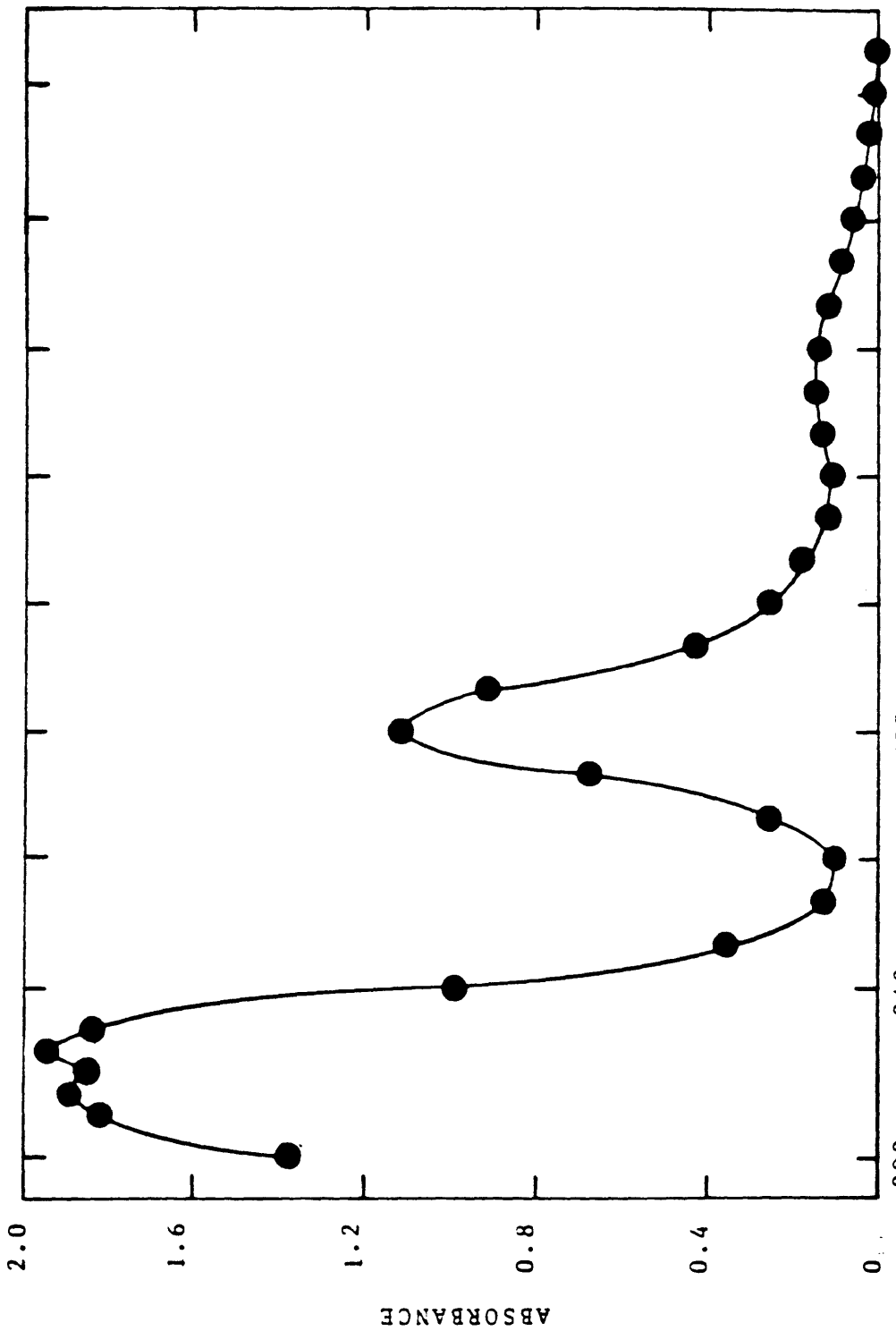


Figure 6. UV-Spectrum of Unpurified PVX-2000

A solution containing PVX-2000 was acidified (pH=1) and after 3 hours its spectrum obtained (Fig. 7). The peaks at 227, 302 and 382 nm vanished and only a peak at 212 nm remained (Fig. 7). It is known (54,55) that at low pH xanthates decompose into carbon disulfide, alcohol and potassium hydroxide. Therefore, the peak at 212 nm is attributed to carbon disulfide. However, it is reported that (55) carbon disulfide absorbs at 206.5 nm.

The ultraviolet spectrum of purified synthesized PVX-2000 is shown in Fig. 8. The peaks at 227 and 302 nm correspond to xanthate. It is important to point out that in this spectrum (fig. 8) only the peaks corresponding to xanthate were obtained. This means that the purification of PVX-2000 was succesful. Also, it is important to point out that PVA does not have absorbance in the ultra-violet region.

3.2.2 INFRARED SPECTRA

Infrared spectra of PVA and purified PVX-2000 were obtained and are shown in Figs. 9 and 10. Absorption band assigments have been made (40,57) for PVA. If these assigned bands are compared with the PVA spectrum obtained in this work, possible assignment can be made (Table 5). The PVA used in this work was 75% hydrolyzed. This means that

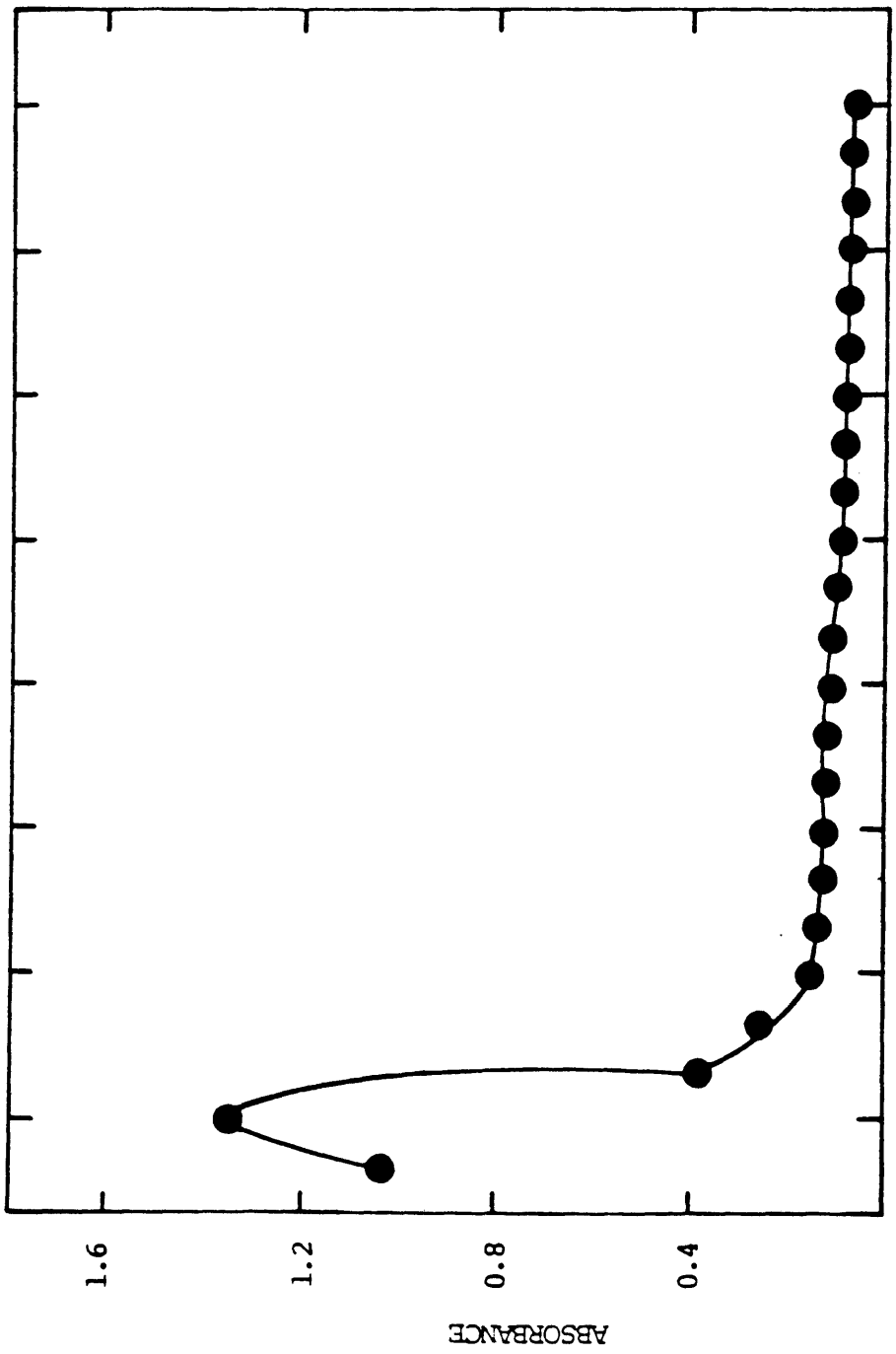


Figure 7. Variation in ultra-violet spectrum of unpurified PVX-2000 solution after acidification to pH = 1

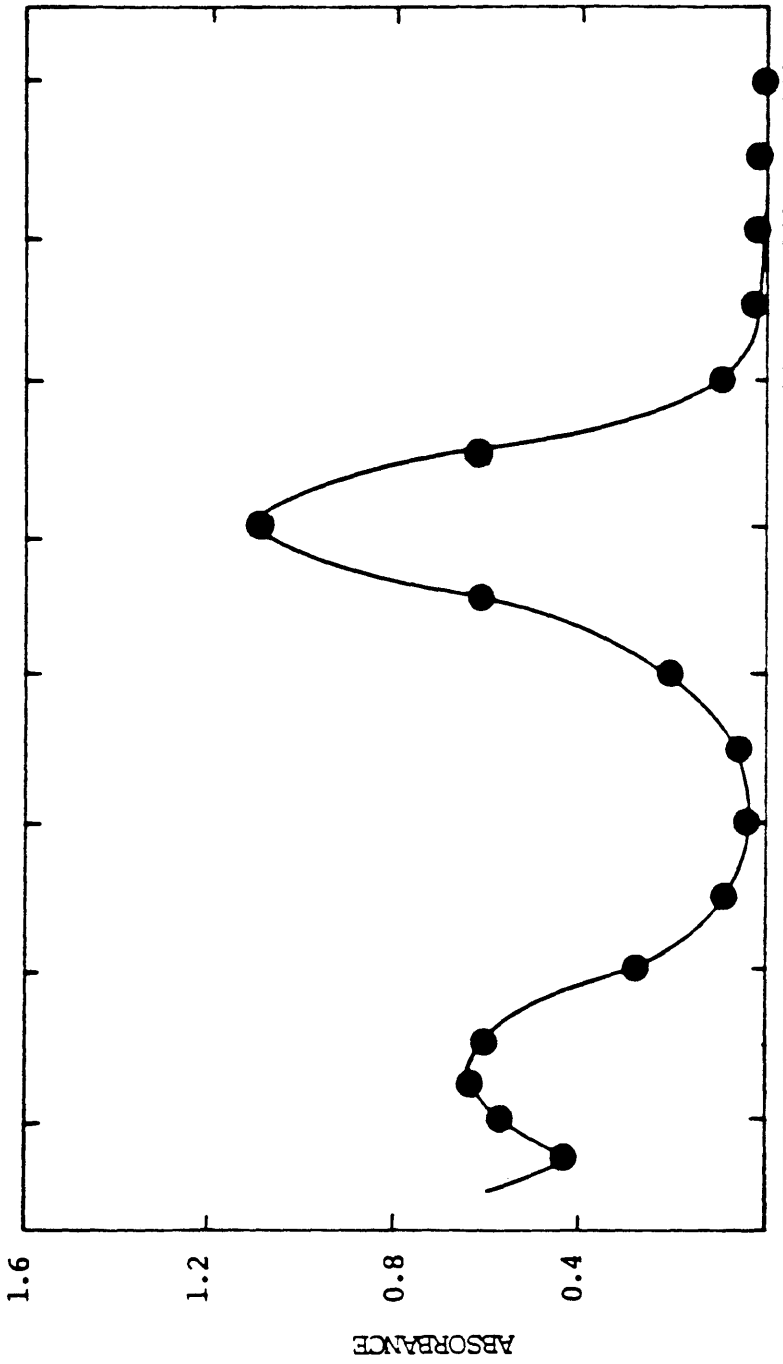


Figure 8. UV-Spectrum of purified PVX-2000

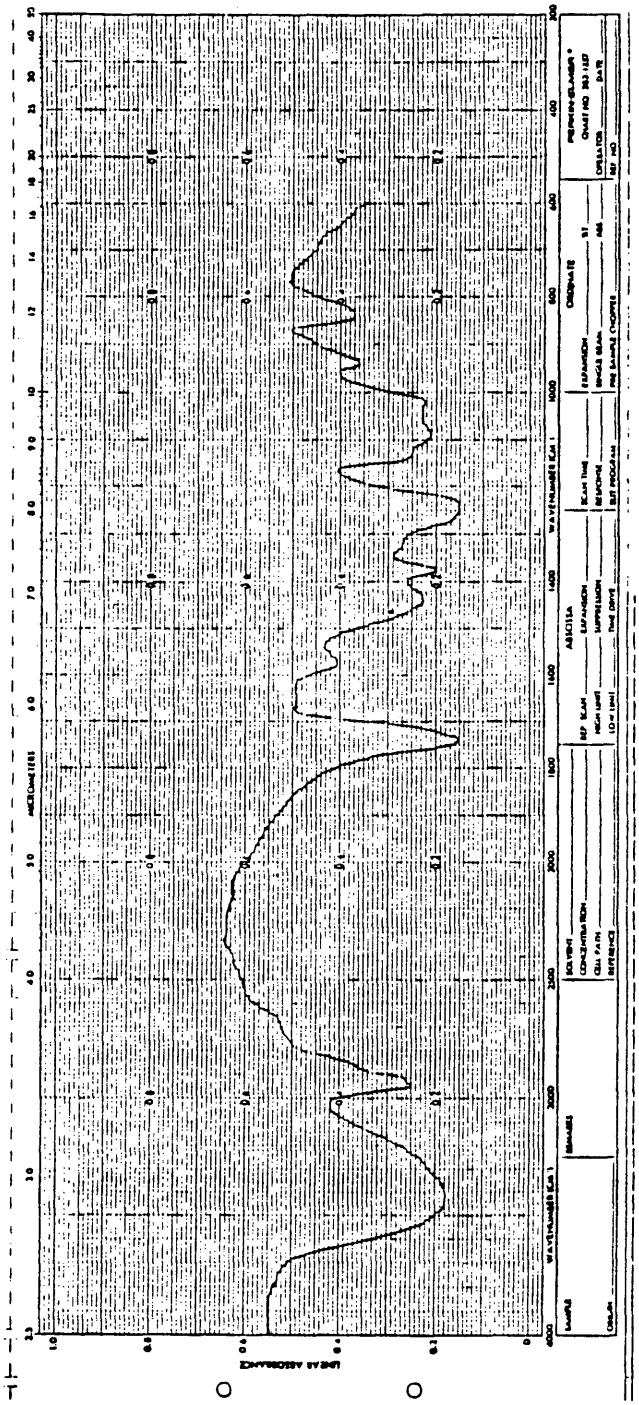


Figure 9. Infrared spectrum of polyvinyl alcohol (PVA)

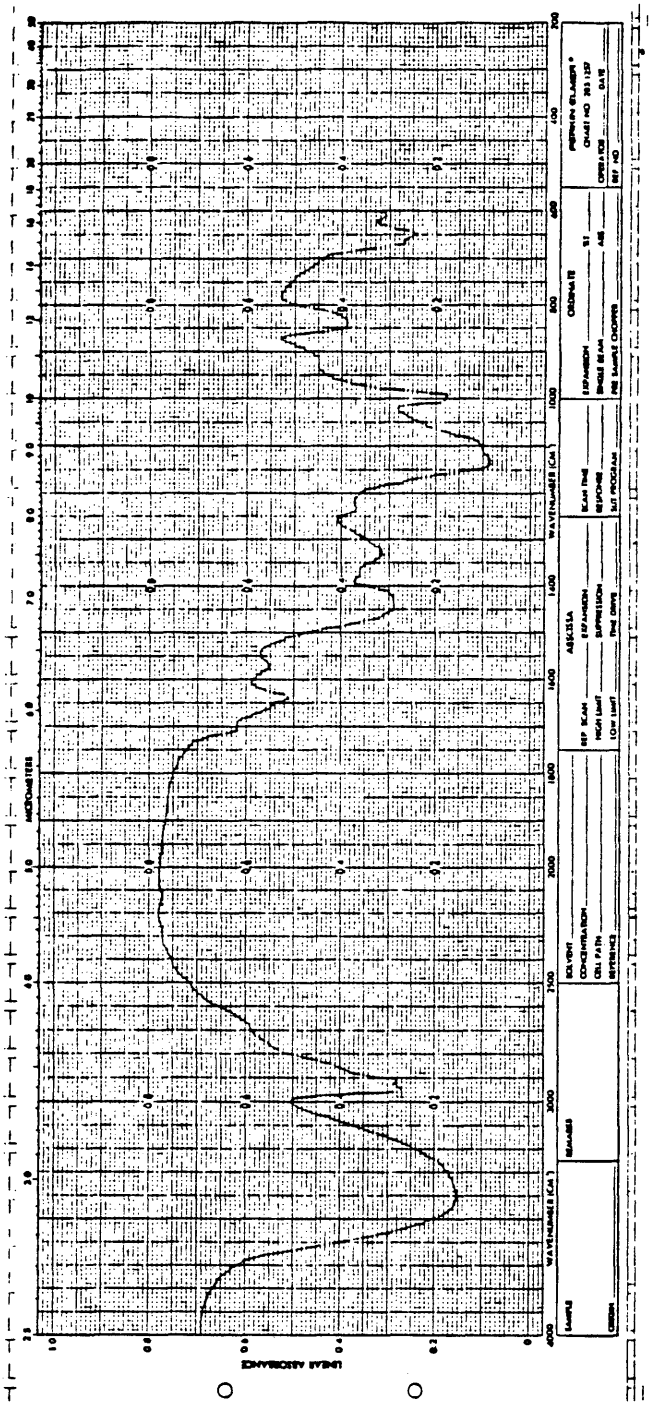


Figure 10. Infrared spectrum of purified PVX-2000

Table 5. Frequencies and possible assignments (50, 59) of PVA and PVX-2000 Frequencies are given in cm^{-1}, weak (w), moderate (m), moderate strong (ms), and very strong (vs)

PVA	PVX-2000	ASSIGNMENTS
3400 (vs)	3400 (vs)	O-H stretching
2930 (vs)	2940 (vs)	C-H stretching
1740 (vs)	1640 (m)	C=O vibration
1570 (m)	1570 (w)	
1440 (m)	1440 (m)	O-H,C-H bending
1375 (m)		C-H wagging
	1325 (w)	C-H,O-H bending
1250 (m)		CH_3-COO
	1240 (m)	C-H wagging
	1140 (vs)	C=S vibration
	1090 (w)	C-OH stretching
	1000 (vs)	C-O vibration
940 (m)	940 (w)	
830 (s)	830 (s)	CH_2- rocking
	650 (s)	O-H twisting

the PVA is partially hydrolized or some acetate groups have been left in the product. This fact is in agreement with the spectra recorded, which are similar to the polyvinyl (alcohol + acetate) spectra reported in the literature (57).

Fig. 10 shows the infrared spectrum of purified PVX-2000 and Fig. 11 compares the spectrum of PVA with that of PVX-2000. The spectrum of PVX-2000, with the exception of the 1000-1200 cm^{-1} region, looks like the spectrum of PVA reported in the literature (57).

The spectrum of PVX-2000 (Fig. 11) at 1200-1000 cm^{-1}, in comparison with PVA spectrum (Fig. 9) shows two distinct strong vibrational modes occurring at 1000 and 1140 cm^{-1}. The absorption band at 1000 cm^{-1} is attributed (48) to C=O vibration and the absorption band at 1140 cm^{-1} to C-S vibration. However it seemed that C=O and C-S vibration were slighty shifted from 1143 to 1140 cm^{-1} and from 1055 to 1000 cm^{-1} respectively.

Reference to the spectrum of PVA also shows that the synthesized PVX-2000 no longer contains an acetate group; this may be due to the purification carried out.

Fig. 12 shows the generalized assignment of the infrared absorption bands used in this work.

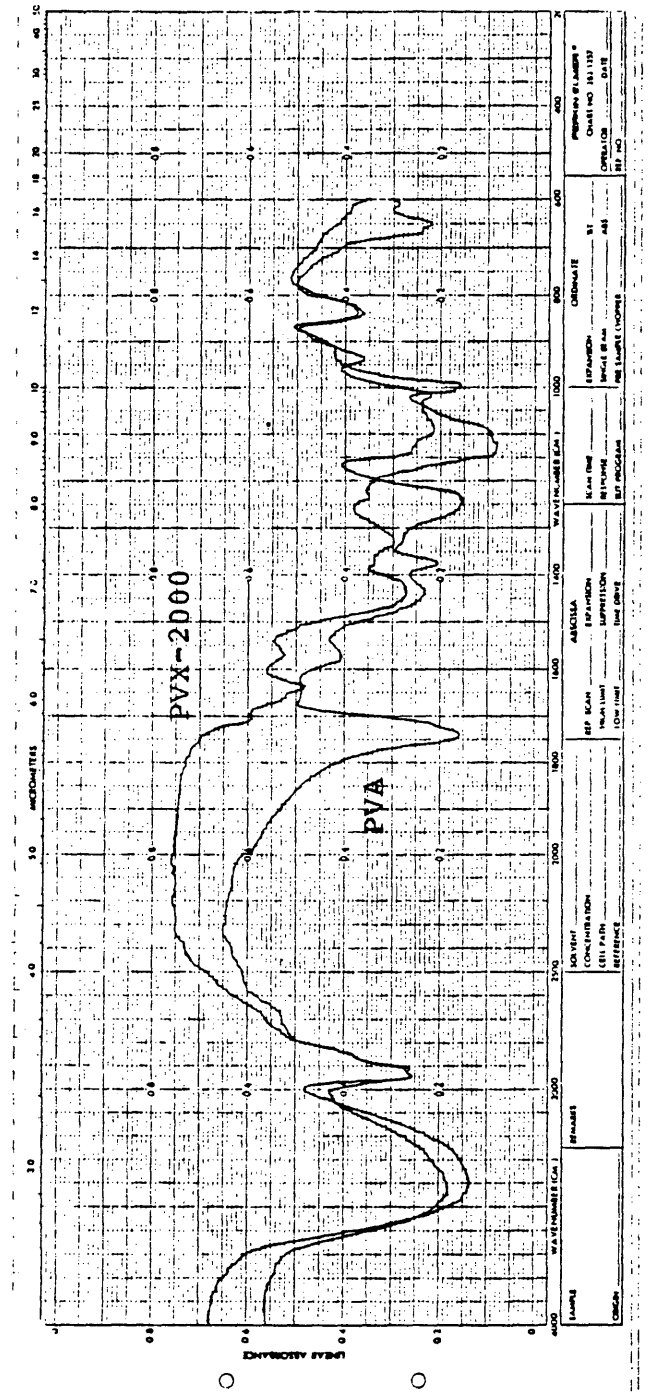


Figure 11. Infrared spectra of purified PVX-2000 and PVA

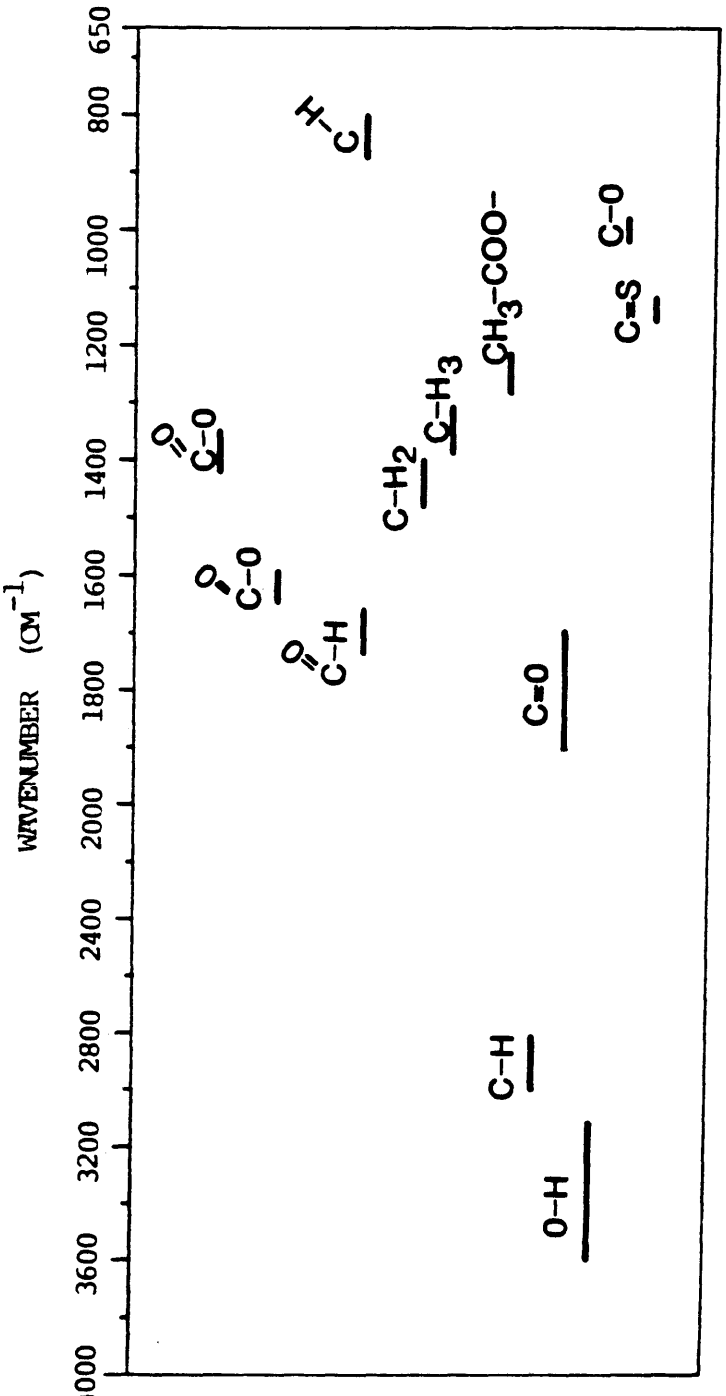


Figure 12. Assignments of infrared absorption bands

3.3 DEGREE OF XANTHATION

Bushell and Malnarich (46) were the first to apply spectrophotometry to the measurement of xanthate quantities in flotation liquors, and Shauenstein and Theiber (58) were the first authors to report a spectrophotometric method for xanthate determination. They reported that the wavelength of the maximun absorption (301 nm) and the molar absorptivity (ε) at 301 nm were not significantly affected by the hydrocarbon group attached to the xanthate group ($-OCSS^-$). These results were confirmed by others (56,59), including Maurice and Mulder (60), who made an extensive statistical study of the absorbance of solutions of potassium ethyl xanthate. The absorbance at 301 nm was used as a measure of xanthate concentration.

Fig. 13 shows the calibration line used in this work for ethyl xanthate. It was obtained by plotting absorbance values at 302 nm for various concentrations of ethyl xanthate. Each point of absorbance is an average of 4 values. The line shows that Beer's law holds up to 14 ppm.

Ethyl xanthate was purified by the recrystallization of a commercial sample. The method used has been described by Dewitt and Roper (61). Xanthate was added to acetone at 40 ^{o}C on a water bath and stirred for a few minutes; some of the solids did not dissolve and this undissolved

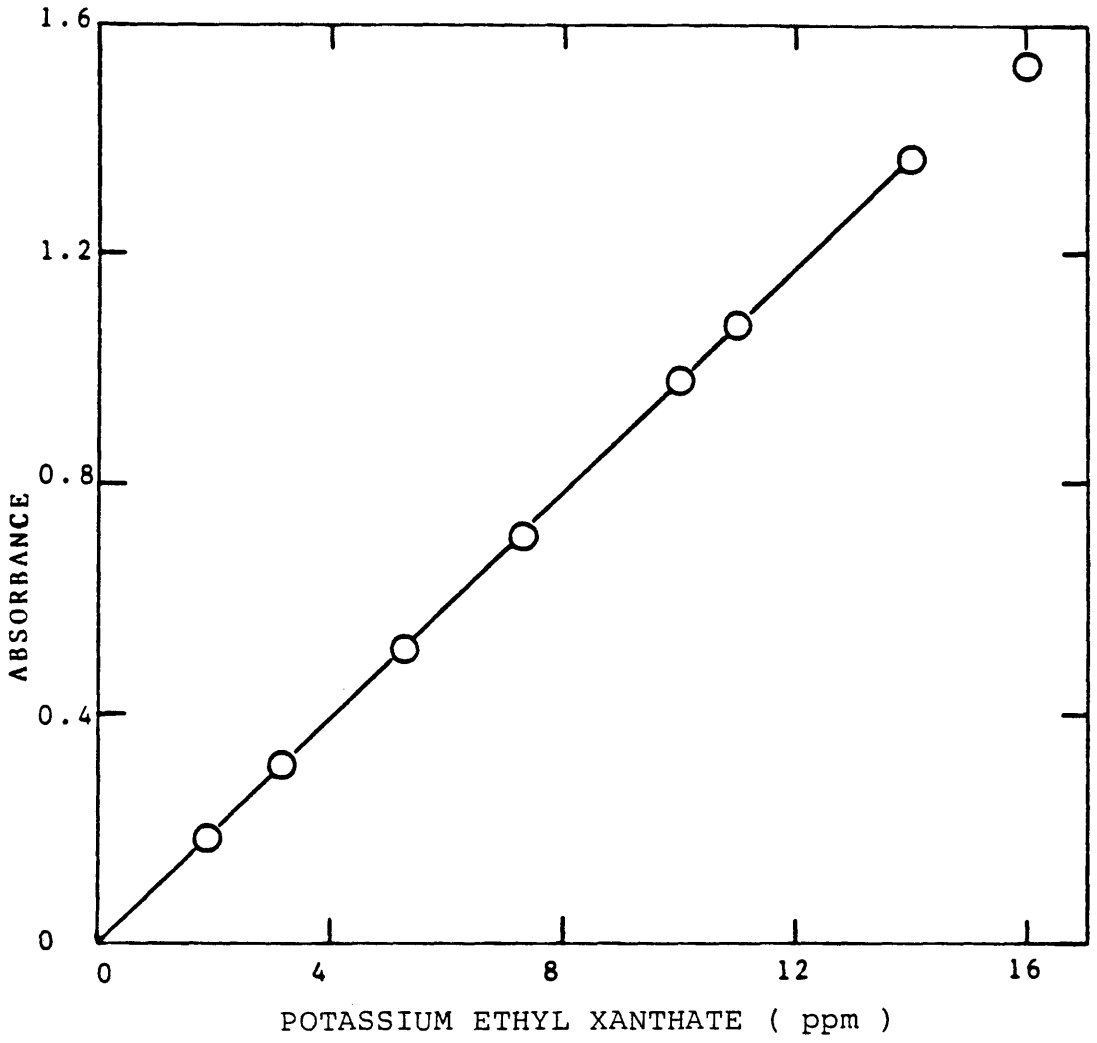


Figure 13. Calibration line for potassium ethyl xanthate in water (wavelength 302 nm)

portion is quite different from the rest; it is the same kind og impurity found in the commercial xanthate. It was filtered out and discarded. To the cold filtrate benzene was added slowly while stirring, and the precipitate was filtered by suction. The precipitate was then dissolved again in acetone, and petroleum ether was added rapidly with no stirring. The precipitate thus obtained was again recovered by filtration and washed with petroleum ether. It was then transferred to a vaccum desiccator containing a small beaker of concentrated sulfuric acid and small amount of recently heated active charcoal on a watch glass (presumably to absorb petroleum ether vapors) and was kept under vacuum for at least 12 hours. This method produced xanthate of 99% purity and virtually free from all side reaction products.

Fig. 14 shows the calibration line obtained with the purified synthesized PVX-2000. The line shows that Beer's law holds up to 200 ppm. Purified PVX-2000 was used to obtained the absorbance values at 302 nm for various concentrations.

It is considered that xanthate groups are randomly distributed among vinyl alcohol groups of PVA. The oldest method (50) for the quantitative determination of xanthate based on the quantitative oxidation of xanthate to

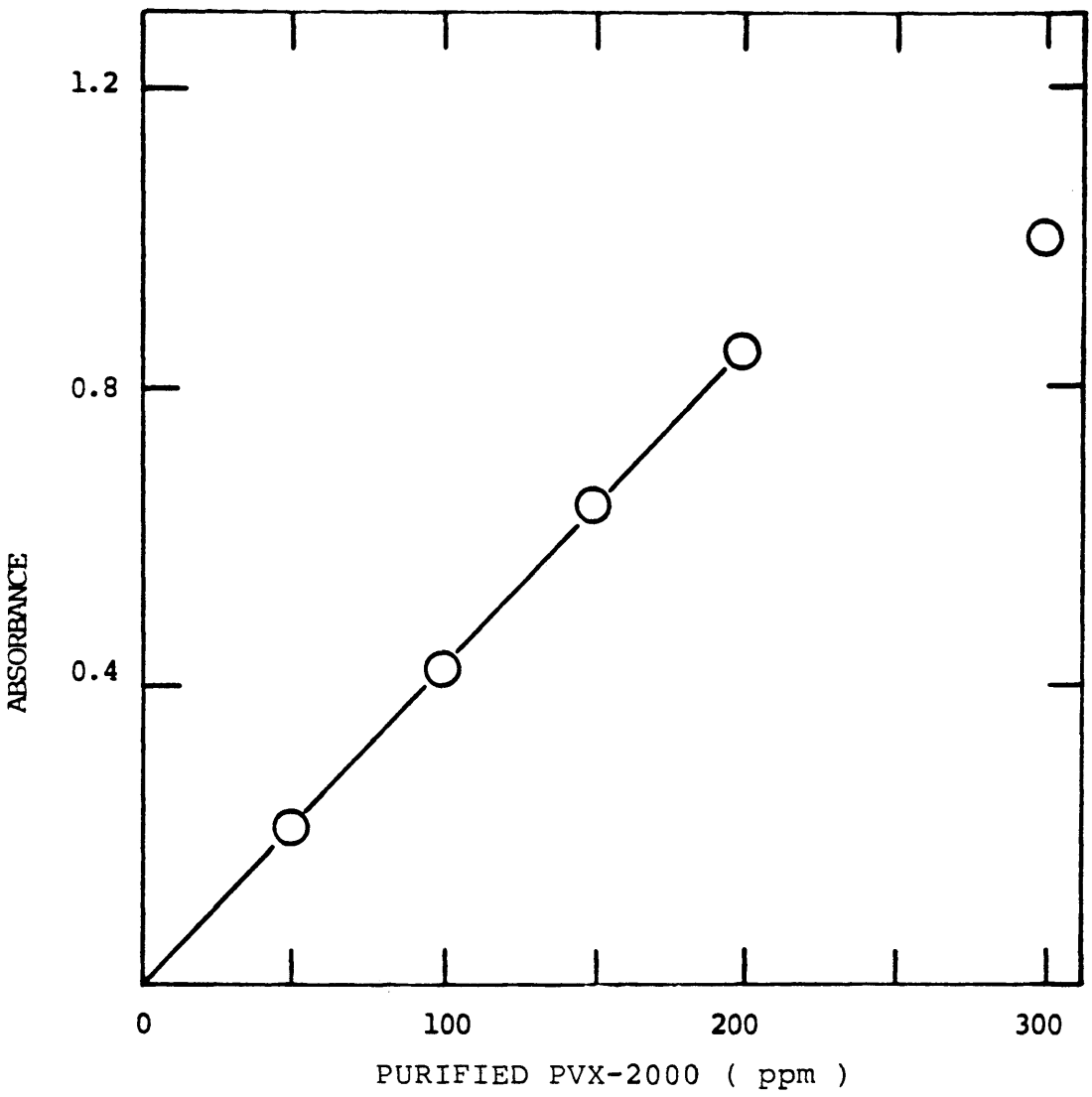


Figure 14. Calibration line for purified synthesized PVX-2000 in water (wavelength 302 nm)

dixanthogen by iodine was first used. But it was found that the PVA reacts with iodine, giving the characteristic blue color at the end point. This was in agreement with the work reported in the literature (40,62).

The spectrophotometric method was used to determine the xanthate incorporated in the PVA.

The calibration line obtained for commercial xanthate (Fig. 13) was used for the calculation of the degree of xanthation.

The absorbance at 302 nm was measured at different PVX-2000 concentrations. The calibrations lines of PVX-2000 prepared under different conditions of synthesis are presented Fig. 15.

From Fig. 15 may be noted that as the concentration of potassium hydroxide and carbon disulfide increase the slopes of lines increase. This indicates that there is a relationship between the concentration levels of potassium hydroxide and carbon disulfide with the degree of xanthation.

The degree of xanthation in relation to the concentrations of potassium hydroxide and carbon disulfide is summarized in Table 6 (calculations in appendix 2).

It has been reported in the literature (53,55) that the addition of a metal carbonate to the reaction slows down

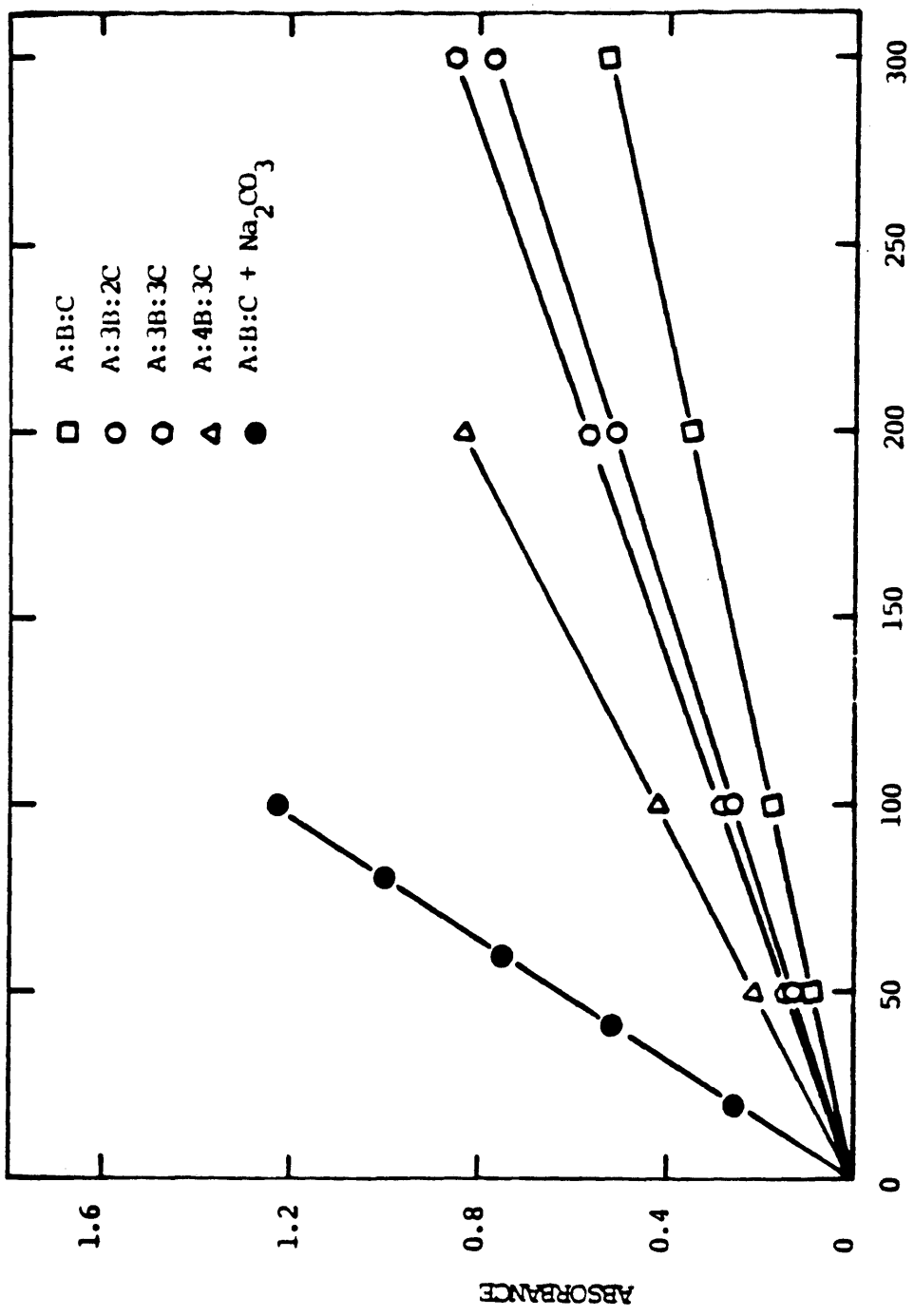


Figure 15. Variation in absorbance of purified PVX-2000 with change in potassium hydroxide and carbon disulfide concentration during synthesis, A = PVA, B = potassium hydroxide, C = carbon disulfide (wavelength 302 nm)

Table 6. Degree of Xanthation

Stoichiometry	PVX-2000 (mg)	Absor-bance	Xanthate (mg)	Degree of Xanthation
A:B:C	50	0.09	0.64	2.2%
A:3B:2C	50	0.13	0.83	2.9%
A:3B:3C	50	0.15	1.00	3.5%
A:4B:3C	50	0.22	1.4	5.0%
A:B:C + Na_2CO_3	50	0.62	4.40	14.1%

Where: A = Polyvinyl Alcohol
B = Potassium Hydroxide
C = Carbon disulfide

the descomposition of xanthate. Sodium carbonate was added in the synthesis of PVX-2000 and the PVX-2000 to which sodium carbonate was added, shows the highest degree of xanthation. The 14.1% of degree of xanthation or the relation of 7 vinyl groups for one xanthate obtained seem to be sufficient to change the PVA properties. Most of the commercially produced cellulose xanthate (15) has a degree of xanthation of about 16.7 % of the number of reactive OH-groups, which is sufficient to change the cellulose polymer properties completely.

3.4 SINGLE MINERAL FLOCCULATION BY PVX-2000

Flocculation of mineral suspensions using PVX-2000 was studied as a function of suspension pH and polymer dosage. Emphasis was placed in this part of the study to obtain conditions for selective flocculation of a single mineral from its mixture with other minerals.

Flocculation response of pyrite by PVX-2000 (10 ppm) at different pH values is shown in Fig. 16. Pyrite is observed to flocculate at pH 11. Fig. 17 shows the flocculation response of pyrite at pH 11 with PVX-2000. Three regions can be identified in Fig. 17: underdose where flocculation is imcomplete, optimal dose, and overdose, where partial restabilization of the flocculated slurry

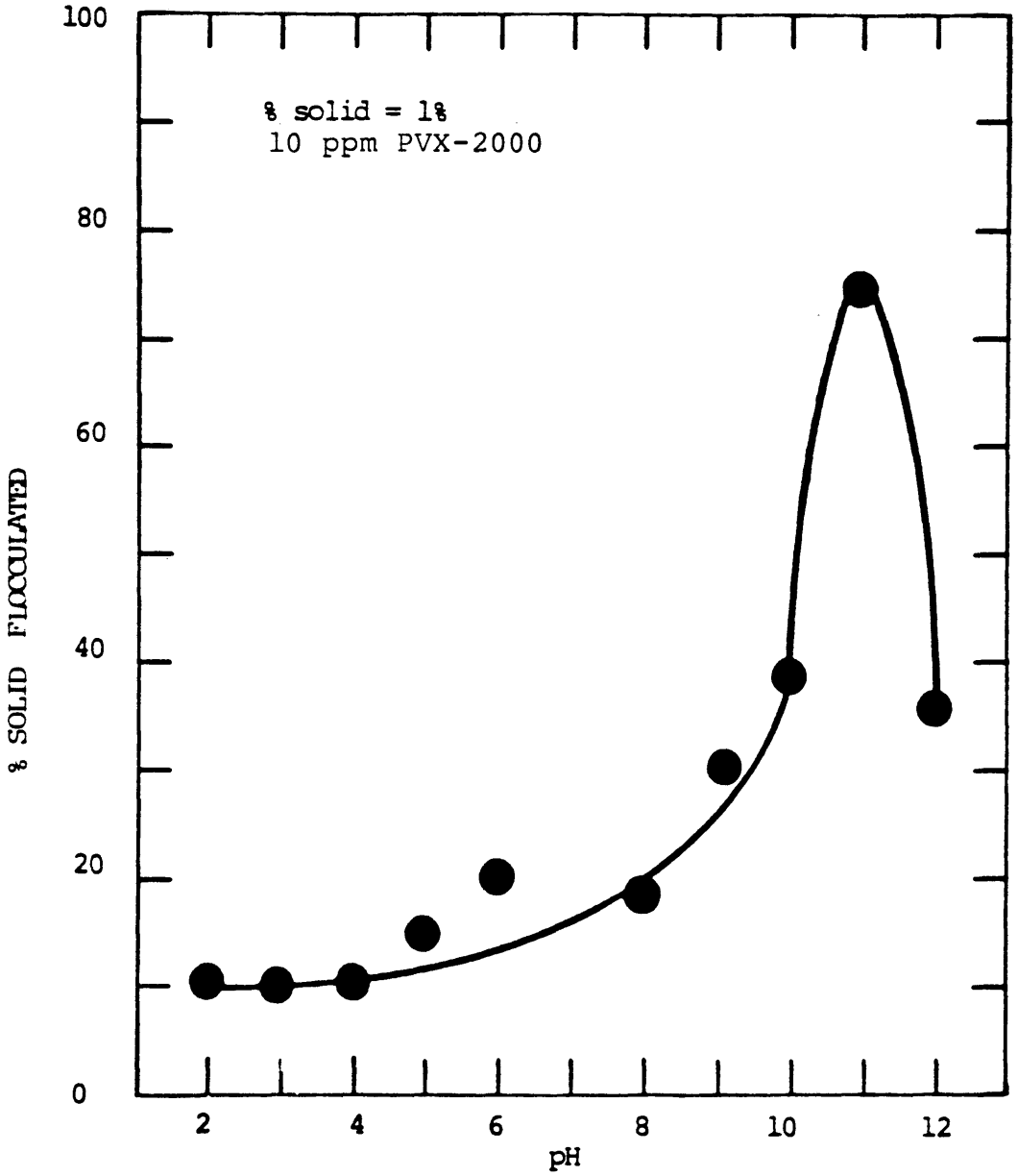


Figure 16. Effect of pH on the flocculation of pyrite by PVX-2000

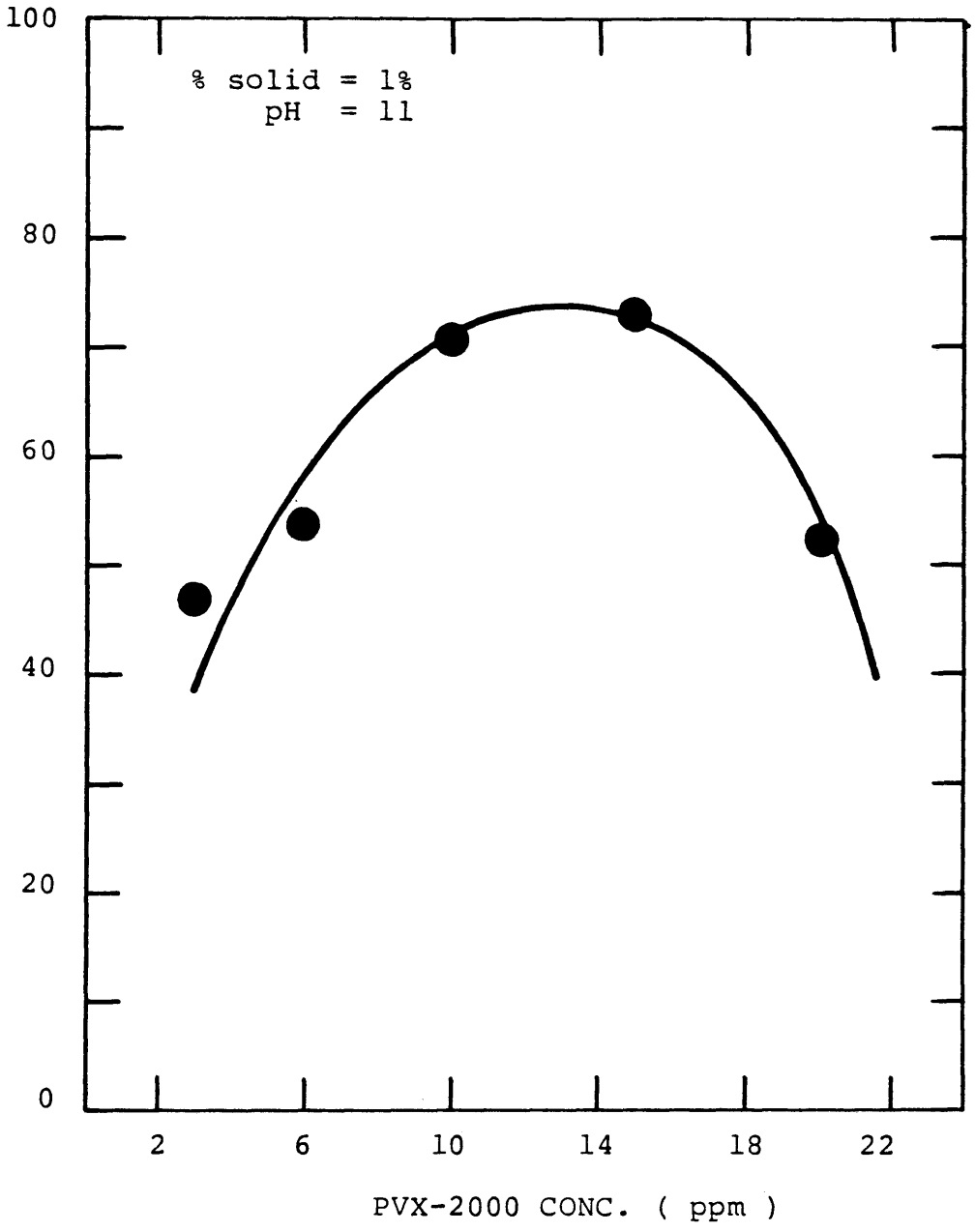


Figure 17. Flocculation of pyrite as a function of PVX-2000 concentration at pH = 11

takes place.

Fig. 18 shows the flocculation response of galena by PVX-2000. It can be seen that the optimun pH at which galena flocculated is about 3. 10 ppm of polyvinyl xanthate was optimal for flocculation of galena at this pH (Fig. 19).

Flocculation response of chalcopyrite using PVX-2000 is shown in Fig. 20 as a function of pH. It can be observed that flocculation of chalcopyrite is least effective in comparison with flocculation of pyrite and galena. The optimal pH is 9, although flocculation is of limited extent. Flocculation of chalcopyrite by PVX-2000, at pH 9, against polymer concentration is shown in Fig. 21. Optimal concentration is 6 ppm.

Flocculation response of quartz by PVX-2000 is shown in Fig. 22. The line obtained indicate that PVX-2000 does not flocculate quartz. Selective adsorption of xanthate in sulfide minerals such as galena is well known in flotation, and it is observed that the difference in flocculation between the sulfide minerals used and quartz occurs for similar reasons.

3.5 SELECTIVE FLOCCULATION OF MINERAL MIXTURES

Separation tests on synthetic mixtures of pyrite/quartz, galena/chalcopyrite, galena/pyrite based on

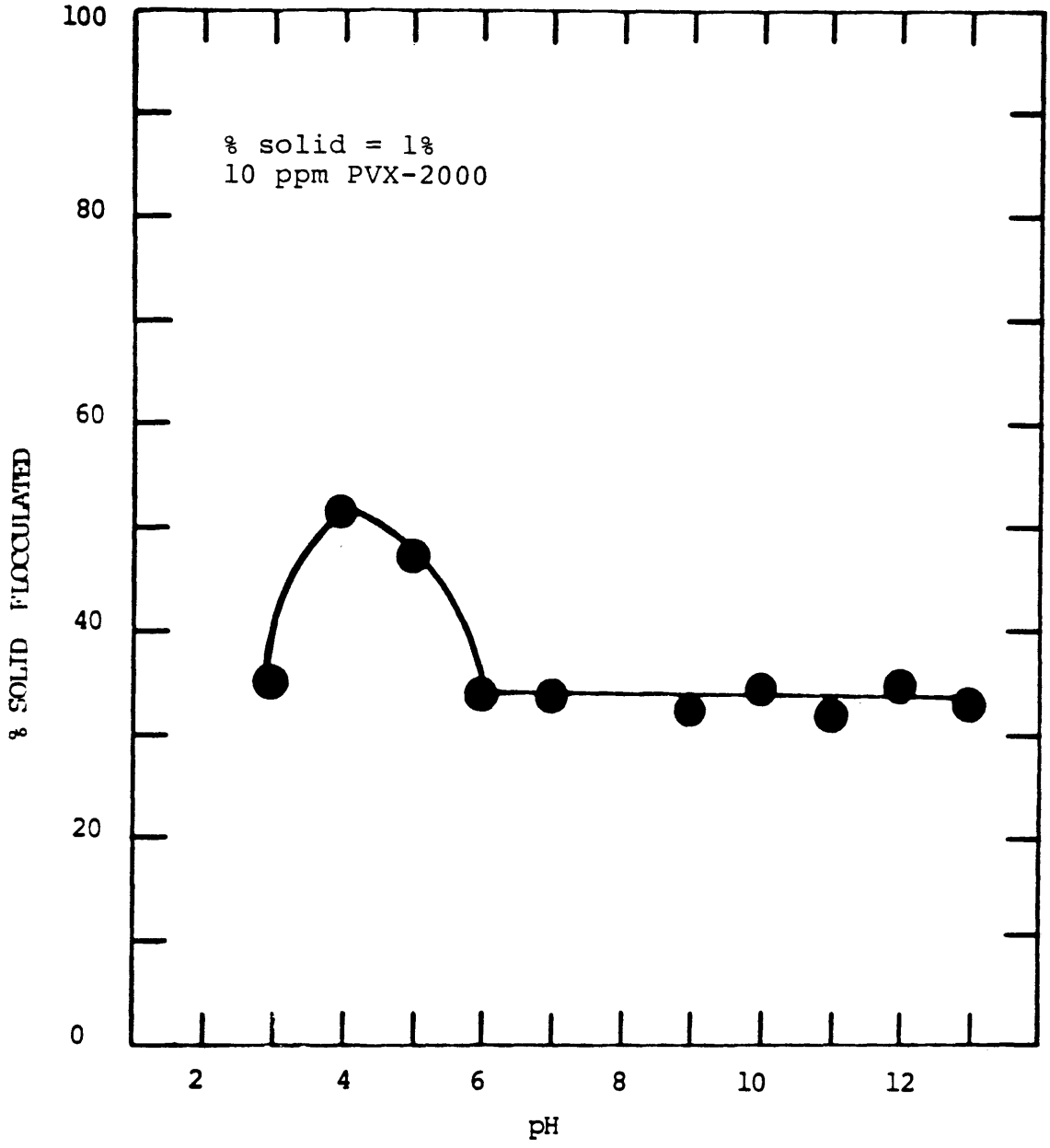


Figure 18. Flocculation of galena by PVX-2000 as a function of pH

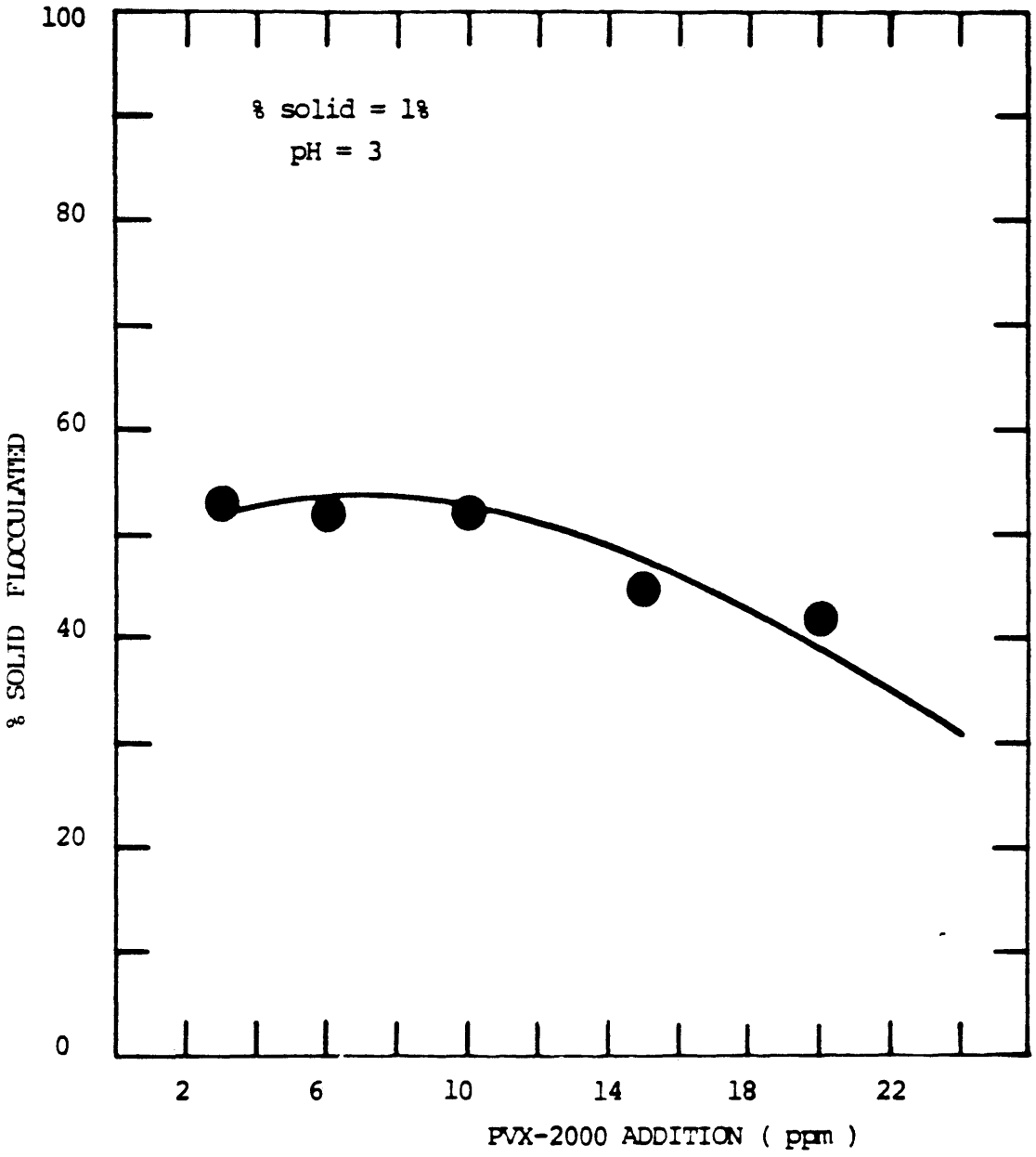


Figure 19. Flocculation of galena as a function of PVX-2000 concentration at pH = 3

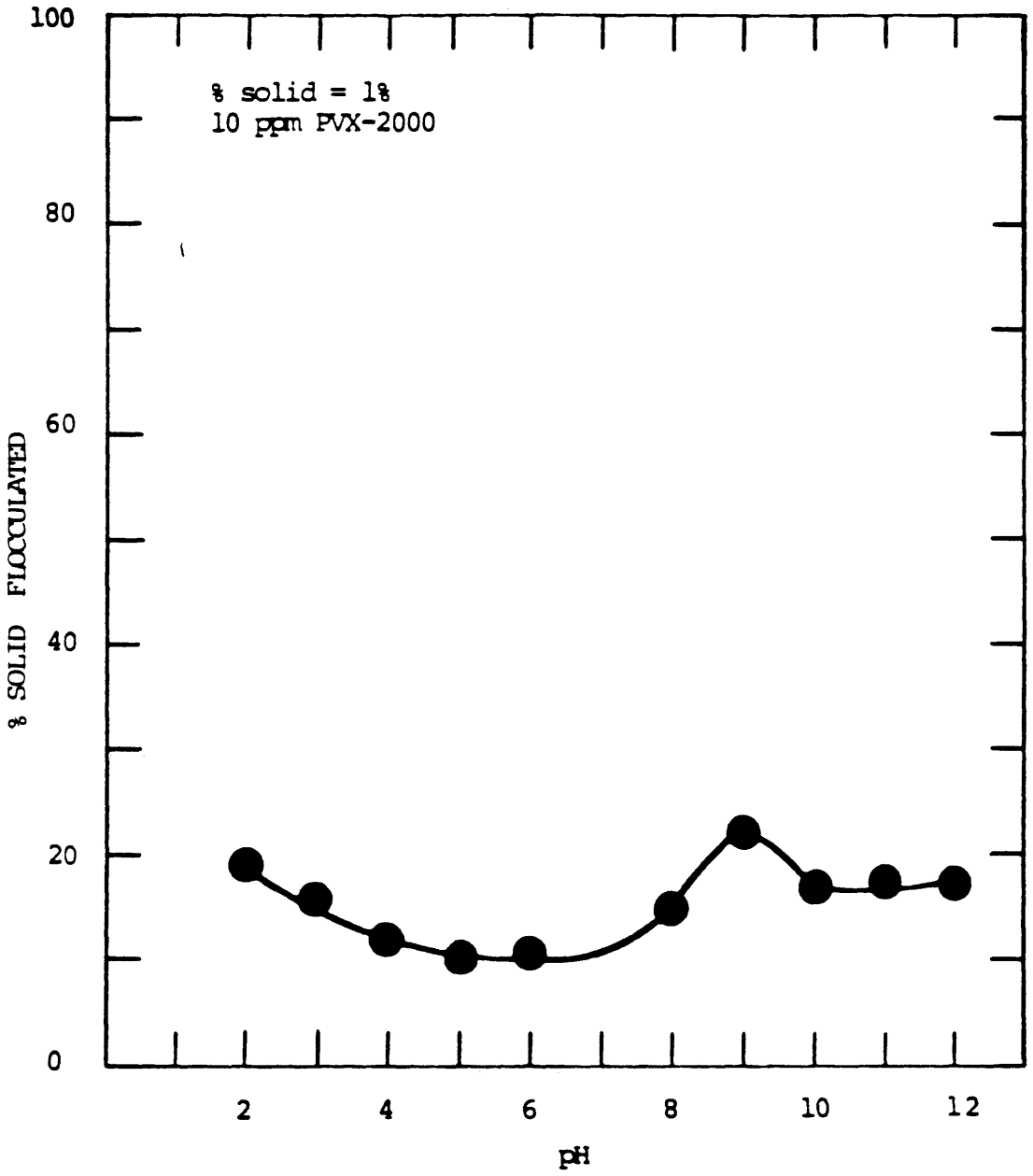


Figure 20. Effect of pH in the flocculation of chalcopyrite by PVX-2000

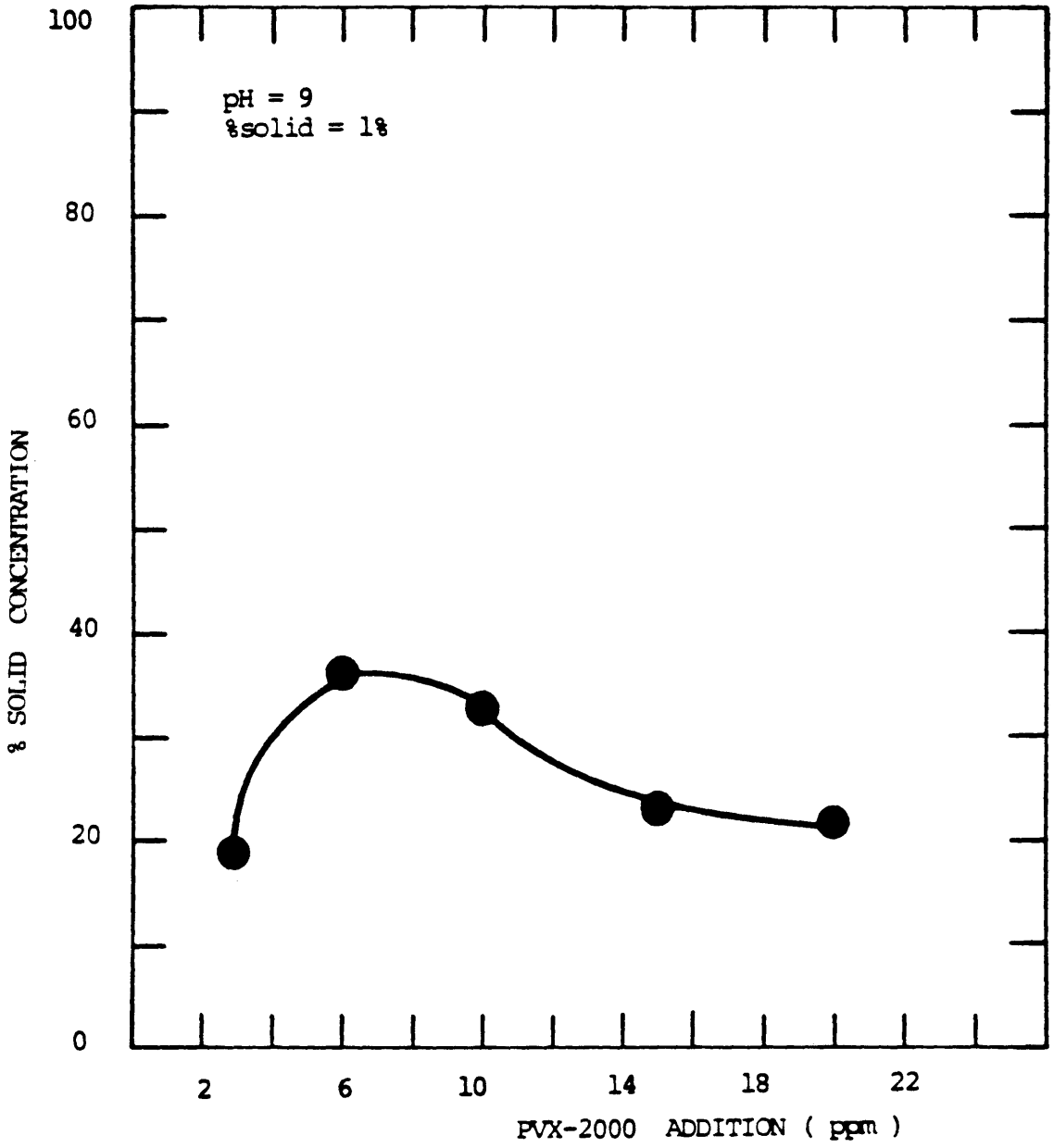


Figure 21. Flocculation of chalcopyrite as a function of PVX-2000 concentration at pH = 9

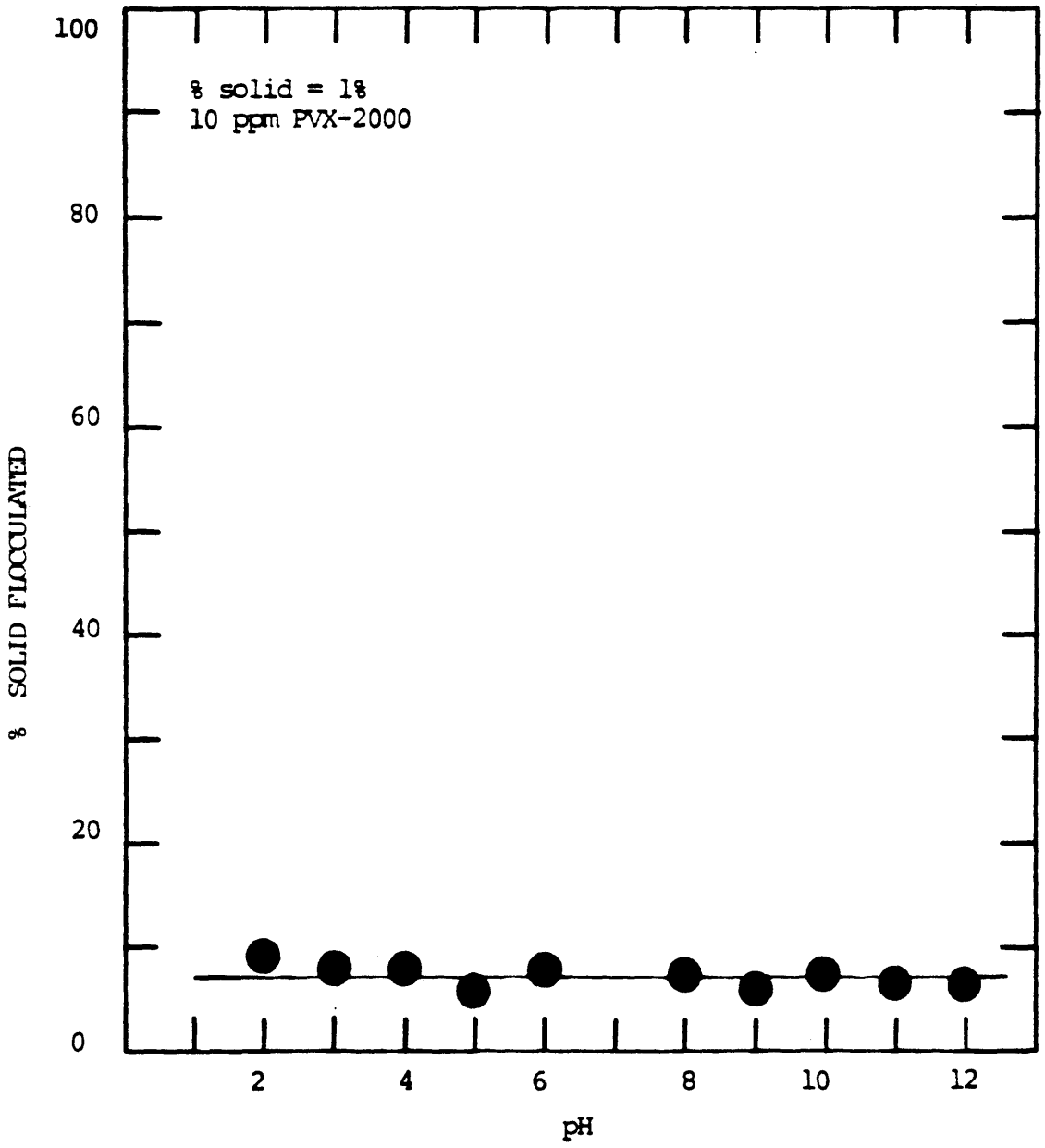


Figure 22. Flocculation of quartz by PVX-2000 as a function of pH

the results obtained using single mineral suspensions were also carried out.

To investigate the selectivity of PVX-2000 toward pyrite, experiments were conducted using mineral systems of pyrite and quartz with concentration of PVX-2000 as the independent variable. Results given in Fig. 23 suggest that separation of pyrite/ quartz mixtures by selective flocculation is feasible. Both the recovery and the grade in terms of percent of pyrite in the flocculated fraction are given in this figure as a function of concentration of the PVX-2000. The grade of the flocs is seen to increase with polymer concentration initially, attains a maximum, and then decreases in the high concentration range. The recovery reaches a maximum value of about 70%.

The flocculation of galena by PVX-2000 was found to be maximum at pH=3 (Fig. 18). On the other hand Fig. 20 shows that chalcopyrite does not flocculate well at this pH. In order to investigate if selectivity of PVX at pH 3 can be obtained towards galena, experiments were conducted using a mixture of galena and chalcopyrite as a function of concentration of PVX-2000. The results are shown in Fig. 24.

The recovery and grade in terms of percent of galena and percent of chalcopyrite in the flocculated and

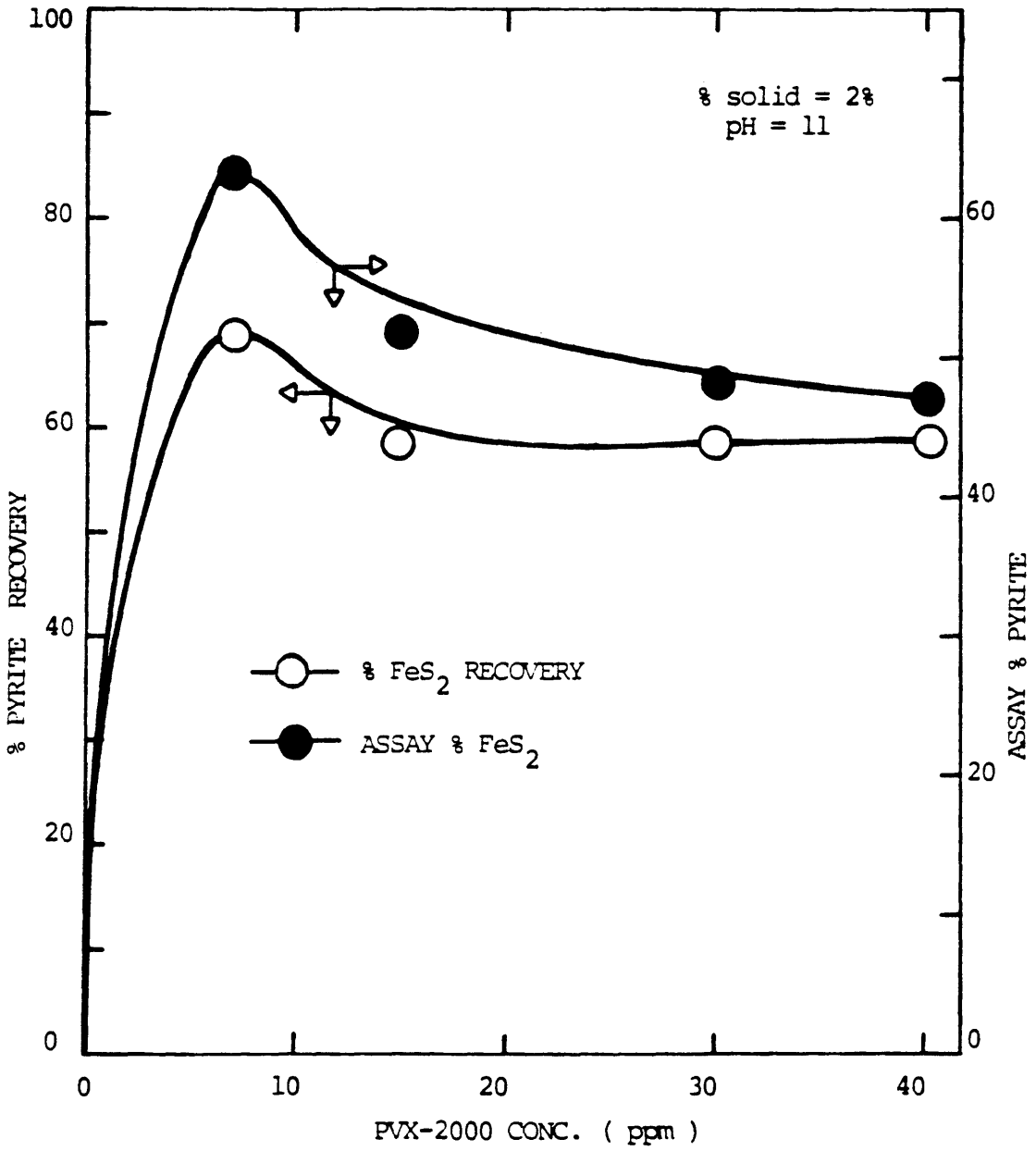


Figure 23. Recovery and grade of the concentrate from selective flocculation of pyrite/quarzt mixture as a function of PVX-2000 concentration at pH = 11

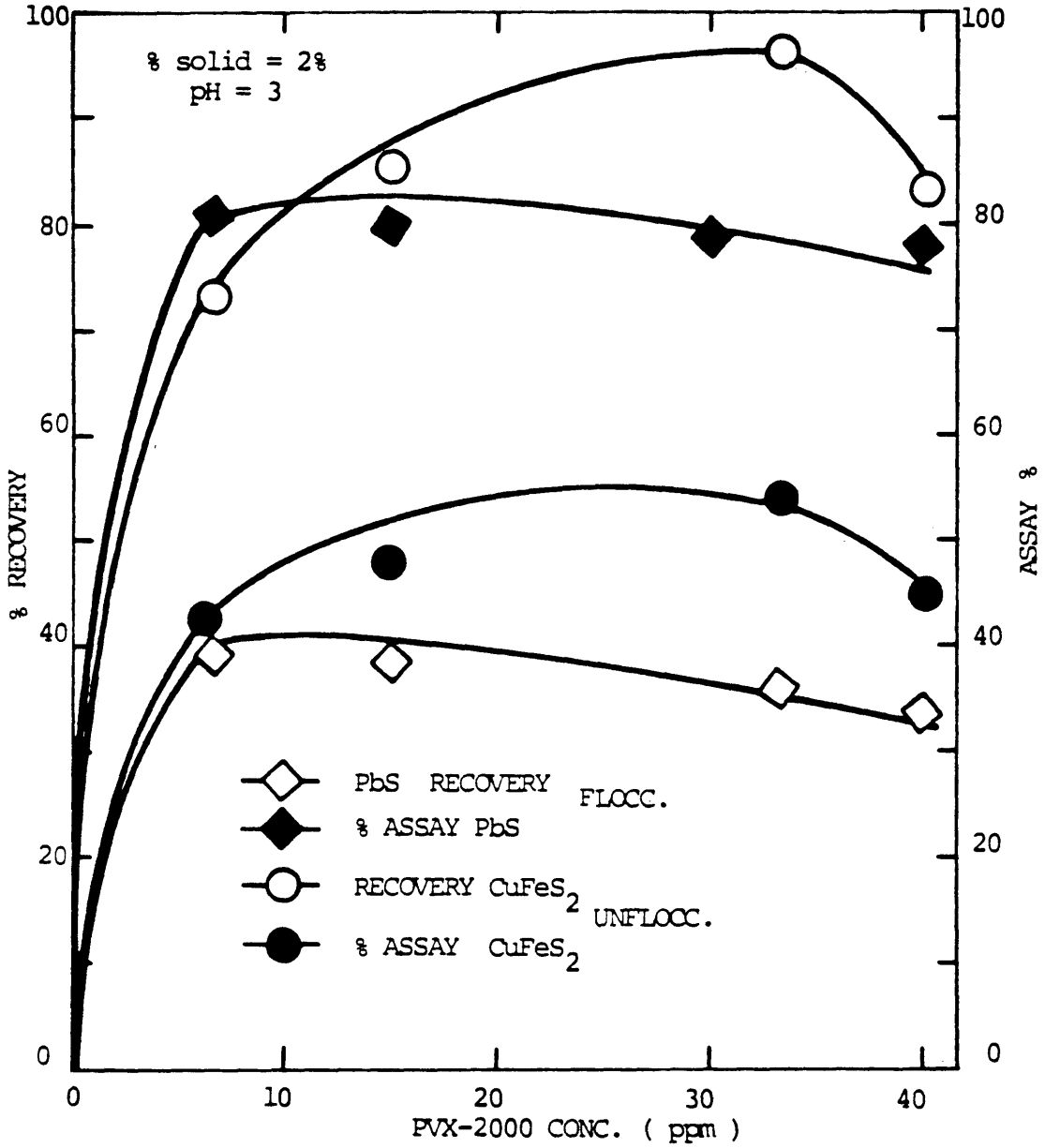


Figure 24. Recovery and grade of the concentrates achieved from selective flocculation of the galena/chalcopyrite mixture as a function of PVX-2000 concentration at pH = 3

unflocculated fractions respectively are also given in Fig. 24 as a function of concentration of PVX-2000. It can be seen that it is possible to obtain a concentrate of galena (flocs) and a concentrate of chalcopyrite (unflocculated) from a mixture containing galena and chalcopyrite.

It was found before that galena alone flocculates at pH 3 and pyrite does not flocculate at this pH with PVX-2000.

To investigate if selectivity can be obtained in the galena/pyrite system, experiments were conducted using mixtures of galena and pyrite with variable concentration of PVX-2000.

Results given in Fig. 25 suggest that separation of galena/pyrite mixtures by selective flocculation is possible. The recovery and grade in terms of percent of galena and percent of pyrite in the flocculated and unflocculated fraction are also given in this figure.

It was observed previously that pyrite flocculated around pH 11 and also it was noted that galena does not flocculate well at this pH.

Flocculation response of a galena/pyrite mixture at pH 11 against PVX-2000 is shown in fig. 26. Results obtained indicate poor separation.

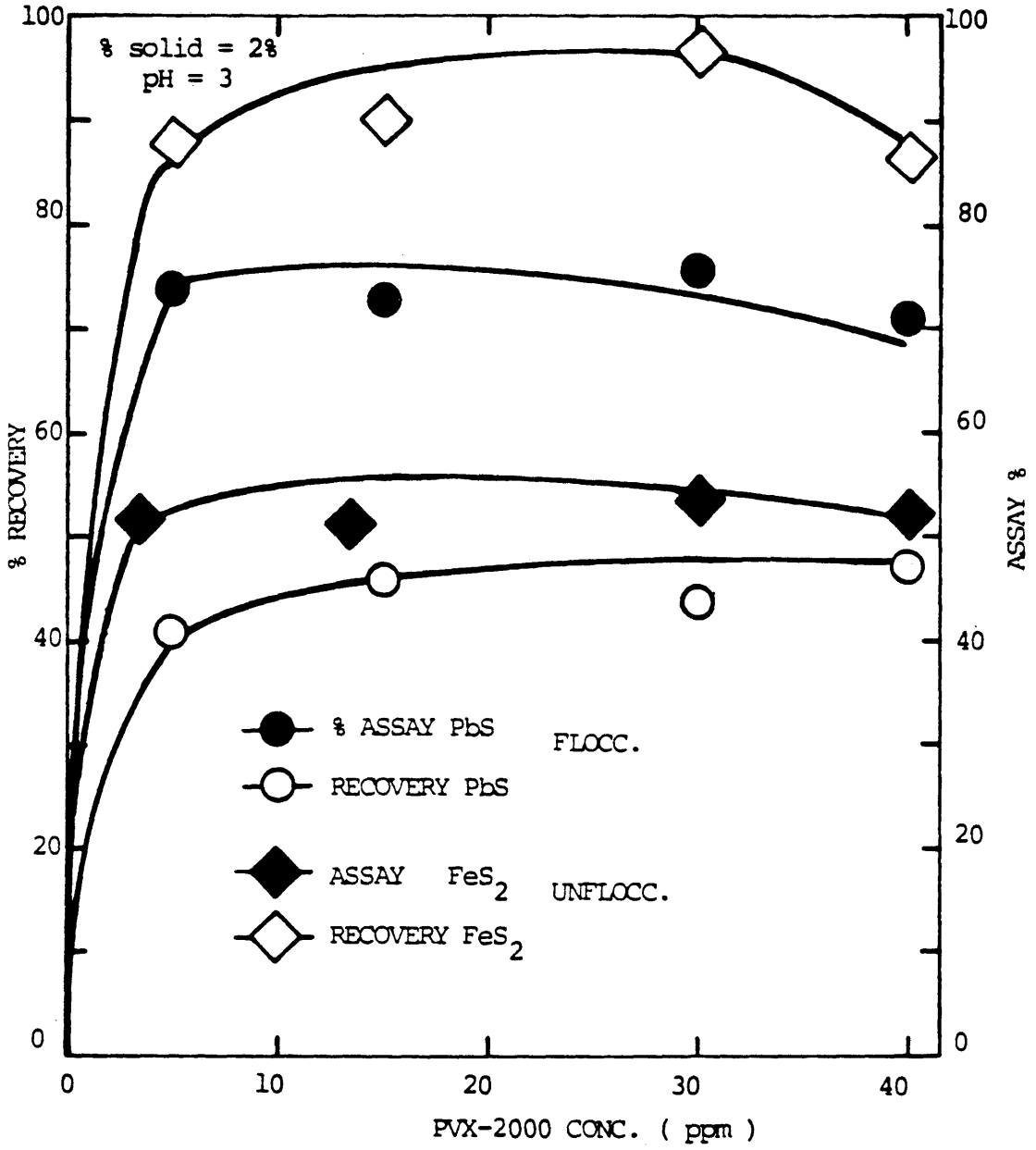


Figure 25. Recovery and grade of the concentrates from selective flocculation of the galena/pyrite mixture as a function of PVX-2000 concentration at pH = 3

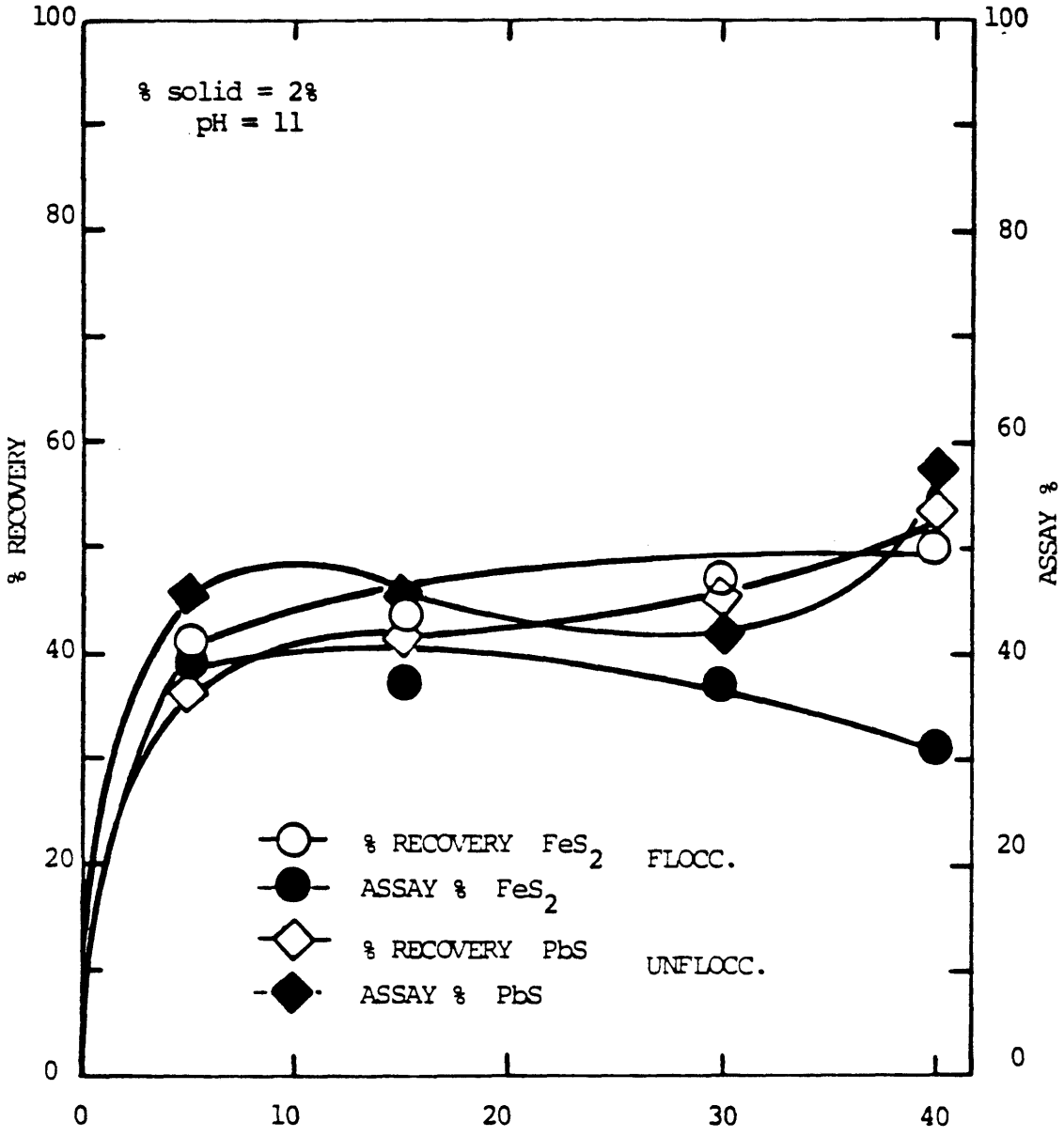


Figure 26. Recovery and grade of concentrates from selective flocculation o galena/pyrite mixture as a function of PVX-2000 concentration at pH = 11

IV. CONCLUSIONS

4.1 SUMMARY

From the data presented the following conclusions were drawn:

1. A polyvinyl xanthate (PVX-2000) flocculant can be synthesized by partial substitution of xanthate groups to a polyvinyl alcohol (PVA) polymer backbone.

The optimal conditions where maximal yield was obtained were as follows:

Mol. Wt. of PVA = 2000

CS_2/PVA = 1.7

CS_2/KOH = 1.3

PVA/KOH = 0.78

PVA/Na_2CO_3= 2.5

Reaction time: alcoholate = 2 hours

xanthation = 6 hours

2. From the characterization (ultraviolet and infrared spectroscopy) technique employed, it can be concluded that PVA had reacted with potassium hydroxide and carbon disulfide to attach xanthate group to a PVA backbone. The ultraviolet spectrum of purified synthesized PVX-2000 shows

a peak at 302 nm which is recognized as corresponding to xanthate group absorption. Inspection of the infrared spectrum of purified synthesized PVX-2000 shows two strong absorption bands at 1140 and 1000 cm^{-1}, which are attributed to C=S and C-O vibrations respectively, characteristic of the xanthate structure. Comparison of PVA and PVX-2000 infrared spectra shows the change of PVA spectrum due to its reaction with KOH and CS_2.

3. Iodometric titration can not be used as a technique to estimate the xanthate attached to PVA because iodine reacts with PVA forming polyvinyl alcohol-iodine complexes. Instead, the spectrophotometric technique is used satisfactorily.

4. The 14.1% degree of xanthation obtained is seen to be enough to change the properties of PVA. This is in agreement with most of commercial cellulose xanthate produced which has about 16.7% degree of xanthation, and which is sufficient to change the cellulose polymer properties completely.

5. From results obtained regarding the degree of xanthation of a reaction in which sodium carbonate was added, it can be

concluded that the addition of this compound increases the degree of xanthation. At the present time the role of sodium carbonate in the synthesis of PVX-2000 is unknown.

6. Synthesized PVX-2000 does not flocculate quartz.

7. Flocculation responses of pyrite, galena and chalcopyrite fines to PVX-2000 were determined for single mineral systems. It was established that pyrite, galena and chalcopyrite flocculated at pH 11, 3 and 9 respetively. Optimum dosages are 16, 8, 6 ppm of PVX-2000 concentration respectively.

8. Tests conducted with mixed mineral systems under conditions selected from the above results showed selective flocculation by PVX-2000 to be technically feasible. Thus, pyrite can be selectively flocculated from a mixture of pyrite/quartz at pH 11. Also it is possible to obtain a concentrate of galena (flocs) and a concentrate of chalcopyrite (unflocculated) from a mixture containing galena and chalcopyrite at pH 3. Separation of galena/pyrite mixtures by selective flocculation is also possible at pH 3.

4.1 RECOMMENDATION OF FUTURE WORK

The work done in this research was using PVA with an average molecular weight of 2000. It has been shown that xanthate can be attached to backbone of this PVA. More work needs to be done with PVA of higher average moleclar weight. The relationship between molecular weight and degree of xanthation needs to be investigated.

The synthesized PVX-2000 needs to be tested in flocculation tests with more sulfides minerals, in order to discover the scope of it is selectivity. The relationship leading the entrapment need to be established.

V. REFERENCES

1. Somansundaran, P., and Fuerstenau, D.W., Editors, "Reports on Proc. of Workshop on Research Needs in mineral Processing" Submitted to NSF, Columbia Univ. New York, 1975.

2. Collins, D.N., and Read, A.d., "The Treatment of Slimes", Minerals Sci. Eng. 3(2),19, 1971.

3. Yarar, B., "Polymer Flocculants and Selective Flocculation an Overview in Solution and Surfactant Chemistry", Theoretical and Applied Aspects, Editors, K.L. Mittal and E.J. Fendler, Plenum Press 1982.

4. Trahar, W.J., "A Rational Interpretation of the Role of Particle Size in Flotation", Inst. Jour. of Min. Proc., 8, 1981, pp. 289-327.

5. Yarar, B., "Flocculation Process ", Mining Engineering (AIME), vol. 35, 5, May 1983, pp. 466-467.

6. Michaels, A.S., "Aggregation of Suspensions by Polyelectrolytes", Industrial and Engineering Chemistry, vol. 46, , July 1954, pp. 1485-1490.

7. Friend, J.P. and Kitchener, J.A., Filtration and Separation, 9,1, 1972.

8. Villar, J.W., and Gilbert, A.D., Min. Congr. J., 61 (10), 40, 1975.

9. Banks, A.F., "Selective Flocculation-Flotation of Slimes from a Sylvinite Ore", Beneficiation of Mineral Fines, NSF Work-shop, Editors P. Somasundaran and N. Arbiter, AIME 1978. pp. 269-276.

10. Read, A.D., and Hollick, C.T., "Selective Flocculation Technique for Recovery of Fine Particles", Minerals Sci. Engng., 8, 202, 1976.

11. Yarar, B., and Kitchener, J., "Selective Flocculation of Minerals", Inst. Min. Metall. , 79, C23, 1970.

12. Read, A.D., "Selective Flocculation Separations Involving Hematite", Trans. Inst. Min. Metall., 80,

C24, 1971.

13. Lien, H.O., and Morrow, J.G., "Beneficiation of Lean Iron Ores Solely by Selective Flocculation", CIM Bulletin, October 1978, pp. 109-120.

14. Attia, Y.A., and Kitchener, J.A., "Development of Complexing Polymers for the Selective Flocculation of Copper Minerals", Proc. XIth Int. Min. Proc. Cong., Cagliari, Italy, 1975.

15. Attia, Y.A., "Synthesis of PAMG Chelating Polymers for the Selective Flocculation of Copper Minerals", Int. J. Mine. Process., vol 4, No.3, 1977, pp. 191-208.

16. Rubio, J., and Golfarb, J., "Separation of Chrysocolla from Quarzt by Selective Flocculation with Polyacrylamide-Type Flocculants", Trans. Inst. Min. Metall., 84, C125, 1975.

17. Rubio, J., and Kitchener, J.A., "New Bases for Selective Flocculation of Mineral Slimes", Trans. Inst. Min. Metall., 26, C97, 1977.

18. Clauss, C.R.A., Appleton, E.A., and Vink, J.J., "Selective Flocculation of Cassiterite in Mixtures with Quartz Using a Modified Polyacrylamide Flocculant", Int. J. Min. Process, vol. 3, No. 1, 1976, pp. 27-34.

19. Mercade, V.V., "Purification of Quartz-Contamined Clay by Selective Flocculation", U.S. Pat. 3.879.283 (CL 209-5,803d), May 6, 1975.

20. Maynard, R.N., "Rapid, Selective Flocculation of Titaniun Oxide Out of Kaolin Slurries". Ger. Patent 2.329.455, January 3, 1974, U.S. Appl. 263,730.

21. Sheridan, J.J., "Purifying Clay by Selective Flocculation", U.S. Patent 3.837.482 (CL. 209/5; B03d), September 24, 1974.

22. Lifirenko, V.E., and Volova, M.L., "Concentration of High-Iron Content Bochmite Bauxites by Selective Flocculation", Tsvet. Met., vol. 1, 1977, pp. 77-80.

23. Christodoulou, S., "The Posibility of Separation Red Mud by Selective Flocculation", Trav. Com. Int. Etude Bauxites, Alumine Alum., vol. 13, 1976, pp. 321-327.

24. Haseman, J.F., "Selective Flocculation of Colloidal Phosphate Ore in the Presence of Clay", U.S. Patent No. 2,660,303.

25. Davenport, J.E., et al., "Beneficiation of Florida Hard-Rock Phosphate by Selective Flocculation", Indus. & Eng. Chem., vol. 8, No. 4, 1969. pp. 527-533.

26. Pradip, Attia, Y.A., and Fuerstenau, D.W., "The Adsorption of Polyacrylamide Flocculants on Apatites", Colloid and Polymer Sci., vol. 258, pp. 1343-1353.

27. Yarar, B. and Ozgur, T., "Separation of Silica and Magnesite by Selective Coagulation and Flocculation", Filtr. Sep., vol. 13, No. 5, 1976, pp. 443-446.

28. Carta, M. et al., "Investigation on Beneficiation of Ultrafine Fluorite From Latium", Procedings of 11th Int. Min. Proc. Cong., Cagliari, Italy, 1975.

29. Attia, Y.A., "Selective Flocculation: State of the Art Review", SME-AIME 111th Annual Meeting, Dallas, Texas, February 14-18, 1982.

30. La Mer, V.K., and Smellie, R.H., "Flocculation, Subsidence, and Filtration of Phosphate Slimes", J. colloid Science, 11, 1956, pp. 704-709.

31. Crawford, J., and Smith, B.R., J. Colloid Interface Sci., 21, 1966, p. 623.

32. Slater, W.R., and Kitchener, J.A., "Characteristic of Flocculation of Mineral Suspension by Polymers", Discussions. Faraday Soc., 42, 1966, pp. 267-265.

33. Termes, S.C., Wilfong, R.L., and Richardson, P.E., "Insoluble Crosslinked Starch Xanthate as a Selective Flocculant for Sulfide Minerals", AIME Annual Meeting, Dallas, Texas, Feb. 14-18, 1982.

34. Termes, S.C., and Wilfong, R.L., "Chelating Crosslinked Starches as Flocculants for Oxide and Hydroxide Minerals Fines", AIME Annual Meeting Atlanta, Georgia, March 6-10, 1983.

35. Brookes, G.F. et al. "The Selective Flocculation of Coal/Shale Mixture Using Commercial and Modified

Polyacrylamide Polymers", XIV Int. Min. Proc. Cong., Toronto, Canada, October 17-23, 1982.

36. Attia, Y.A., and Fuerstenau, D.W., "Feasibility of Cleaning High Sulfur Coal Fines By Selective Flocculation", XIV Int. Min. Proc. Cong., Toronto, Canada, October 17-23, 1982.

37. Sresty, C. "Beneficiation Of Mineral Slimes: Flocculation & Selective Flocculation ", MSc. Thesis, Columbia University, 1977.

38. Yoshioka, Y., and Nagano, M., "Sodium Xanthate of PVA", Chem. High Polymers (Japan) 9, 1952, pp. 22-27.

39. Nico, A., "Xanthates of PVA and Certain of their Derivatives", Ann. Chim. (Paris), 13, 4, 1957, pp. 145-188.

40. Finch, C.A., "Polyvinyl Alcohol" John Wiley & Sons, 1973.

41. Foster, L.S., "The preparation of Xanthates and Other Organic Thiocarbonates", Utah Eng. Exptl. Sta. Tech., Paper No. 2, 1929.

42. Keskyula, I.Y, "Potassium and Sodium Xanthates", Trans. State. Ints. App. Chem. (USSR), 30, 1936, pp. 29-68.

43. Glembotskii, V.I and Plaskin, I.N., "Flotation, Primary Sources", New York, 1972.

44. Wills, B.A., "Mineral Processing Technology" 2nd. Edition, Pergamon Press, 1981.

45. Kelly, E.G., and Spottiswood, D.J.., "Introduction to Mineral Processing", John Wiley & Sons Inc., 1982.

46. Bushell, C.H., and Malnarich, M., "Reagents Control in Flotation", Trans. AIME, 205, 1956, pp. 774-737.

47. Little, L.H., Poling, G.W, and Leja, J., "Infrared Spectra of Xanthate Compound", Can. J. Chem., vol. 39, 1961.

48. Shankaranayana, M.L., and Patel, C.C., "Infrared Spectra of Xanthate Compound", Can. J. Chem. 39, 745,

1961; 39, 1783-86, 1961.

49. Fritz, F., "Spot Test in Organic Chemistry ", Elsevier, 1956, pp. 67-77.

50. Rao, R.S., "Xanthate and Related Compounds", Marcel Dekker, Inc., New York, 1971.

51. Rosenstein, L., "Xanthate and Tertiary Xanthates", Canadian Paten. 311,334 and 311,335, May 12, 1931.

52. Baudet, G., et al. "Synthesis and Characterization of Selective Flocculants Based on Xanthates Derivatives of Cellulose or Amyloze", Ind. Minerale Mineralurgie, (France), March 1978, pp. 19-35.

53. Jones, W.H., and Woodcock, J.T., "Decomposition of Alkyl Dixanthogen In Aqueous Solution", Int. J. Min. Proc., 10, 1983, pp. 1-24.

54. Hovenkamp, S.G., "Sodium Dithiocarbonate as a By-Product in Xanthating Reactions", J. Polymer Sci: Part C, No. 2, 1963, pp. 341-355.

55. Leja, J., "Surface Chemistry of Froth Flotation", Plenum Press, 1982.

56. Pomianowski. A., and Leja, J., "Spectrophotometric Study of Xanthate and Dixanthogen Solutions", Can. J. Chem., vol. 41, 1963, pp. 2220.

57. Rodriguez, F., "Principles of Polymer System", Mc Graw-Hill Co., 1982.

58. Schauenstien, E and Treiber, E., "Ultra-violet Investigation on Viscose-Spectrophotometric Determination of Xanthate Sulphur and Trithiocarbonate", Melliand Texber., 32, 1951, 43-47.

59. Iwasaki, I., and Cooke, S.R.B., "Absorption Spectra of Some Sulphydryl Compounds", Trans. AIME, 208, 1957, pp. 2219-2230.

60. Maurice, M.J., and Mulder, J.L., "The Ultra-violet Spectrophotometric Determination of Potassium Ethyl Xanthate", Mikrochim. Acta., 1957, pp. 661-667.

61. Dewitt, C.C., and Roper, E.E., "The Surface Relations

of Potassium Ethyl Xanthate and Pine Oil", J. Am. Chem. Soc., 54, 1932, pp. 444-445.

62. Zwick, M.M., "Polyvinyl Alcohol-Iodine Complexes", J. App. Poly. Sci., vol. 9, 1965, pp. 2393-2424.

APPENDIX 1

SELECTIVE FLOCCULATION: 9 RULES OF YARAR & KITCHENER

General Principles:

(1) the mixed pulp must initially be in a dispersed condition so that all the particles are essentially separate.

At least one of the components must form a relatively stable suspension (either inherently or after modification by a dispersing agent). This component is to remain dispersed. Mutual coagulation of minerals with opposite sign of electric charge, which is commom, has to be prevented (see below).

(2) Selective flocculation is based on selective adsorption of the polymer on the different minerals.

This follow because flocculants consist of macromolecular substances which can bind perticles together by bridging the gap between them. They must therefore be (a) highly extended when in solution, and (b) attached by adsorption to the surface of the mineral grains. Since (a) is not dependent on the particles, differences of flocculation can arise only from differences in adsorption,

which, in turn depend on differences of surface chemistry. (3) The surface properties of minerals in mixtures may be different from those of the separate minerals. (4) Modifying agents can be employed to control the properties of the minerals or the flocculants, or both.

Their action, which may lead to "activation" or inhibition of flocculation (by analogy with froth flotation), can fall into one of the following classes.

(a) Alteration of the surface potential of the minerals: for example, anionic polyelectrolytes will not adsorb on to highly negatively charged surfaces unless the surface potential is reduced by means of apropriate electrolytes.

(b) change in the mechanism of adsorption of the polymer: for example, polyvalent cations can act as activators for adsorption of anionic polyelectrolytes.

(c) alteration of the end-to-end dimensions of the polymer.

(d) Change in the degree of ionization of the polymer.

(e) Mutual interaction of polymers, when more than one are used.

(f) Competition between the modifying reagent and the flocculant for surface sites on the minerals: for example, sodium hexametaphosphate prevents the adsorption of anionic

flocculants on calcite. (A different case is the effect of polymer of low molecular weight in stabilizing dispersions against flocculants of high molecular weight.)
(5) As the solids content ("pulp density") of a mixed slurry is increased, an increasing proportion of the component not intended to flocculate is carried down. This effect, which will be called "entrapment", arises inevitably during the rapid formation of a three-dimensional network of flocculated mineral. The voids in the flocs commonly amount to 80-90 per cent and, of course, include dispersed particles, some of which can not escape when the flocs settle down.

There are several important practical consequences of this principle.

(a) The grade of the flocculated fraction (in a one-stage process) is improved by starting with a lower solids content.

(b) Entrapment decreases the recovery of the non-flocculated fraction.

(c) Entrapped material can be freed by gently agitating the flocs in a further quantity of the suspension medium (i.e. by use of a two-stage process the grade can be improved).

(d) In contrast to the requirements for the most rapid

solid-liquid separation, large flocs are not desirable in selective floculation, because large flocs retain entrapped particles too strongly.

(e) Similarly, although it is necessary to produce large enough flocs to secure preferential sedimentation (relative to the unflocculated component), the flocs obtainable with the most effective modern flocculants of very high molecular may be too large (in that they cause excessive entrapment). Instead of reducing floc size by use of less than the "optimun dosage" of such a flocculant, it may be preferable to employ the optimun dosage of less effective flocculant. The lower limit of floc size is set by the necessity for the floc to settle fast faster than the unflocculated componet, but the flocs can be built up slowly by conditioning (see below).

(6) For a given combination of minerals there is an upper limit to the solids content and to the ratio of the components that can be successfully treated with given reagents.

Each component alone has an upper limit of solids content at which it forms a sufficiently stable suspension. Although it may be possible, in principle, to flocculate either the major or minor component, in practice the choice will be determined by (a) which of them forms the

more stable residual suspension, (b) the fact that flocculation of the major component is particularly liable to cause entrapment of the other, and (c) the fact that the formation of flocs of the minor component is greatly hindered by the presence of a large proportion of non-flocculable component. it follows that with a given ore and with given modifying agents, the maximun solids content will be dictated by the above considerations.

(7) With a mixture of minerals of very different specific gravity, it is easiest (though not essential) to affect a separation by flocculating the haevier component; a relatively weak flocculant is adequate, because of the favourable rate of settling of the flocs.

Conversely, it is necessary to flocculate the lighter component, and it should also be one which produces large enough flocs of this component to secure adequate diffrence of settling rates.

(8) As with simple flocculation, efficient selective flocculation requieres an initial uniform distribution of flocculant through the pulp, followed by a period of conditionig at a low rate shear.

Uniform distribution of the flocculant is obtained by a combination of high rate of stirring and addition of flocculant in the form of a dilute solution. the period of

addition can be kept short by use of very high rates of stirring-when fairly concentrated solutions can be used (e.g. 0.1%). This may be an advantage for systems containing relatively soluble minerals or minerals having soluble oxidation products.

A conditioning period is required after addition of the flocculant to allow the flocs to grow by collision of the treated particles. The process is classed as "orthokinetic flocculation", as the particles are brought together by hydrodynamic forces rather than Brownian motion. During this period the shear rate must be kept near an optimun value at which a compromise is reached between the build-up and breakdown of flocs. In any case, the rate must be sufficient to keep the non-flocculated component in suspension , and in practice the flocs settle out under these conditions.

(9) To improve the efficiency of the process-especially with pulps of high solids content, where entrapment is a problem-an additional stage can be introduced in which the settled flocs are gently "worked" to release entrapped particles and to consolidate the flocculated material.

On a laboratory scale, for example, this has been carried out successfully by means of an apparatus consisting of an inclined rotating cylinder, the angle of inclination

and spped of which could be adjusted. After addition of flocculant in a separate mixing vessel, the pulp was transferred to the cylinder and conditioned by slow rotation. The flocs tended to settle on the lower and gently tumble, improving in grade while growing in size.

In difficult cases the above apparatus produced much better results than conventional conditioning with a paddle stirrer; in fact, it succeded in certain cases where complete entrapment was ordinarily obtained.

APPENDIX 2

METHODS OF HYDROLYSIS OF POLYVINYL ACETATE.

Clasification of Methods of Hydrolysis

Methods of hydrolysis of polyvinyl acetate are usually grouped into alkaline hydrolysis, aminolysis, and acidolysis, according to the catalyst used. The following chemical reactions occur:

ALCOHOLYSIS:

$$PV\text{-}OAc + nROH \longrightarrow PV\text{-}OH + ROAC \quad (1)$$

HYDROLYSIS:

$$PV\text{-}OAC + nH_2O \longrightarrow PV\text{-}OH + HOAc \quad (2)$$

DIRECT HYDROLYSIS:

$$PV\text{-}OAc + nNaOH \longrightarrow PV\text{-}OH + nNaOAc \quad (3)$$

AMINOLYSIS:

$$PV\text{-}OAc + nHNR_1R_2 \longrightarrow PV\text{-}OH + nAcNR_1R_2 \quad (4)$$

AMMONOLYSIS:

$$PV\text{-}OAc + nNH_3 \longrightarrow PV\text{-}OH + nAcNH \quad (5)$$

At the same time, the following side reaction also occurs

$$ROAc + NaOH \longrightarrow ROH + NaOAc \quad (6)$$

$$HOAc + NaOH \longrightarrow H_2O + NaOAc \quad (7)$$

A small amount of residual monomer is converted to acetaldehyde:

$$\text{V-OAc} + \text{ROH} \xrightarrow{\qquad\qquad} \text{CH}_3\text{CHO} + \text{ROAC} \qquad (8)$$

$$\text{V-OAc} + \text{H}_2\text{O} \xrightarrow{\qquad\qquad} \text{CH}_3\text{CHO} + \text{HOAc} \qquad (9)$$

APPENDIX 3

ESTIMATION OF DEGREE OF XANTHATION:

From Figure 16:

Taking line A:B:C + Na_2CO_3

To 50 ppm (PVX-2000) correspond to 0.62 absorbance

From Figure 15:

To 0.62 absorbance correspond to 64 ppm xanthate (NaEX)

Therefore:

In 50 ppm of PVX-2000 there is 64 ppm sodium ethyl xanthate

$6.4X10^{-3}$g NaEX X $\frac{92\ g\ OCSS^-}{144\ g\ NaEX}$ = $4.1X10^{-3}$g $OCSS^-$

To $50X10^{-3}$g PVX-200 correspond to $4.1X10^{-3}$g $OCSS^-$

Mol. Wt. PVA = 2000

Mol. Wt. monomer = 44 g/mol

Mol. Wt. $OCSS^-$ = 92 g/mol

Mol. Wt. monomer xant. =158.28 g/mol

O-H groups in PVA $\frac{2000}{44}$ = 45.45 O-H groups

Monomer vinyl alc. 44 g will become 158.28 g after xanthation

45.45 monomer will become 45.45 X 158.28 = 7193 g (full xanthation)

45.45 monomer will contain 45.45 X 92 = 4181 g $OCSS^-$ (full xanthation)

$\frac{4.1X10^{-3}g\ OCSS^-}{50X10^{-3}}$ X 7193 g PVX-2000 = 589.6 g $OCSS^-$

$$\frac{45.45 \text{ O-H groups}}{4181 \text{ g } OCSS^-} \times 589.6 \text{ g } OCSS^- = 6.4 \text{ O-H groups become xanthate}$$

$$\frac{45.45 \text{ Vinyl group}}{6.4 \text{ xanthate groups}} = 7.2 \text{ Vinyl groups/1 xanthate group}$$

$$\% \text{ Degree of xanthation} = \frac{6.4}{45.45} \times 100 = 14.1 \%$$