GEOLOGICAL SURVEY OF CANADA · 1842 ·

GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF ENERGY,
MINES AND RESOURCES

PAPER 70-64

THE ADSORPTION AND COPRECIPITATION OF
SILVER ON HYDROUS OXIDES OF IRON
AND MANGANESE

(Report and 5 figures)

Willy Dyck

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ABSTRACT

   With silver-110 m as a tracer, investigations were carried out
on the adsorption of silver on freshly prepared hydrous oxides of iron
and manganese in the pH region 4-8, and silver equilibrium concentra-
tion range $10^{-4} - 10^3$ ppm. The results fit Freundlich adsorption iso-
therms, and may be explained in terms of hydrogen-silver ion exchange.
They also show that adsorption is essentially complete in less than 5
minutes and is strongly dependent on pH and the manner in which the
precipitate was prepared, but is independent of temperature in the
0-50° C range, of moderate concentrations of sodium nitrate (~ 10 g/l),
and of trace concentrations of sodium chloride ($\lesssim 1$ ppm) during test
periods ranging from 1 to 3 days.

   Tests also showed that under equilibrium conditions and simi-
lar chemical environments the amounts of silver coprecipitated or
adsorbed were identical.

   Natural hydrous oxide precipitates adsorb much larger amounts
of silver than do laboratory preparations under similar conditions of pH
and equilibrium silver concentrations due to the presence of ions which
form insoluble salts with silver.

THE ADSORPTION AND COPRECIPITATION OF
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AND MANGANESE

INTRODUCTION

The hydrous oxides of iron and manganese found in nature contain considerable quantities of trace elements such as Ag, Co, Ni, etc. (Boyle, 1965, 1968; Boyle et al. 1966, 1967; Pontus, 1955; Bonatti and Joensun, 1966). It is generally accepted that adsorption plays a dominant role in concentrating trace elements in these oxides. A number of useful empirical rules or laws have been formulated as a result of adsorption experiments using radiotracers (Hahn, 1936). The well known adsorption equations by Freundlich and Langmuir are useful in presenting adsorption data graphically. More recent reviews of adsorption studies of ions from solution and hydrous oxides have been presented by Zhabrova and Egorov (1961), Ross (1963), Amphlett (1964), and Starik (1959).

Ion exchange phenomena observed in adsorption studies have been described by mass action type equations derived from thermodynamic considerations by Guggenheim (1944), Krishnamoorthy, et al. (1948), and others. Several of these derivations were tested by Krishnamoorthy and Overstreet (1950), using clay, clay minerals, and ion exchangers and ions of the alkaline and alkaline earth groups. They found satisfactory agreement between experiment and theory provided H^+ is not one of the exchanging ions. Double layer theory arguments have been employed by Helmy (1963), Heald et al. (1964), and Shainberg and Kemper (1967), to develop equations describing adsorption on clay minerals. These arguments require a knowledge of the nature of the surface of the adsorbent, as well as a number of such basic experimental quantities as ionic radii, hydration-, polarization-, and potential energies of the ionic species, zeta potentials of the dispersed adsorbent, etc.

Among the first to relate adsorption of divalent ions on hydrous ferric oxide to the H^+ concentration employing the law of mass action was Kurbatov et al. (1948, 1951). Anderson (1956) interpreted the effect of pH on zeta potentials of magnetite suspensions in terms of a weak basic dissociation of surface groups. Egorov and Lyubimov (1969) have shown that cations such as strontium are sorbed from aqueous solutions by manganese dioxide by the replacement of not only hydrogen ions but also potassium and manganese (II) ions of the solid phase.

The nature of hydrous oxides of iron and manganese has been studied extensively by Weiser (1935, 1950) and Dey and Gosh (1948). The adsorption of silver on ferric oxide gels has been studied by a number of Russian scientists (Kargin et al., 1939, 1940; Chernikova and Gapon, 1949; Dmitrienko et al., 1951; Dmitrienko and Ryabinia, 1953; Glazman et al., 1958). The silver concentration range investigated by these workers is indicated by the
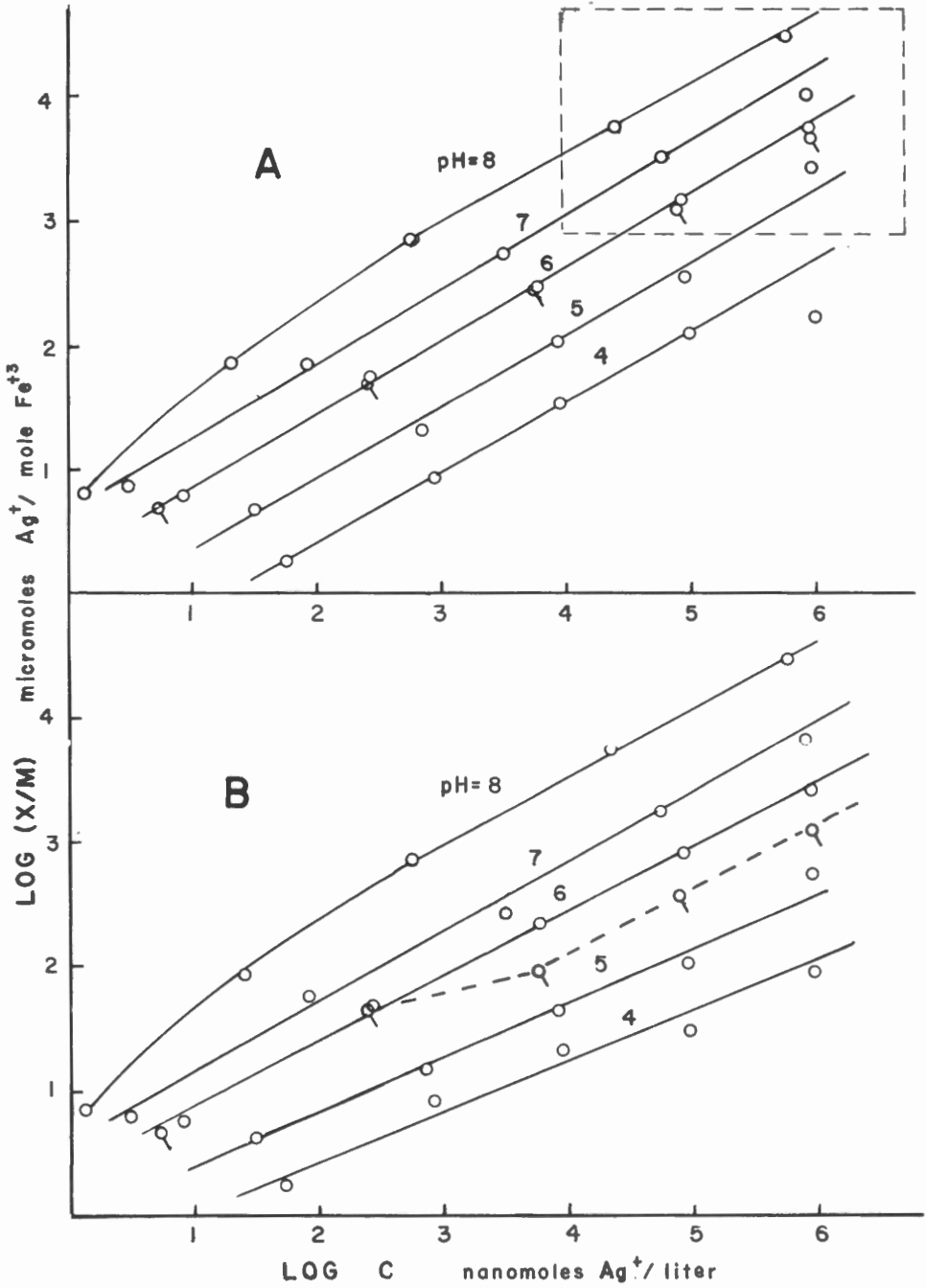
Figure 1. Room temperature (~25°C) adsorption isotherms of silver and hydrous ferric oxide prepared with sodium hydroxide. A - solution measurements; B - washed precipitate measurements. (For details of tests see experimental section.) Points with tail were obtained without $NaNO_3$.

dotted rectangle in Figure 1A. In general their results show that silver adsorption is strongly influenced by the presence of anions which form insoluble silver salts; the less soluble the salt the greater the adsorption. A detailed investigation of the adsorption of silver on freshly prepared hydrous ferric oxides in the silver concentration range and pH range encountered in natural waters has been carried out by Dyck (1968). The adsorption of metallic ions including silver by air dried manganese dioxide was studied by Chatterji and Dhar as early as 1923. The analytical chemistry of aqueous manganese oxides has been summarized by Morgan and Stumn (1965).

This report summarizes experimental adsorption and coprecipitation data obtained using silver, tagged with Ag-110m, as the adsorbate and freshly prepared, as well as natural hydrous oxides of iron and manganese as adsorbents.

EXPERIMENTAL PROCEDURES

The adsorption tests with iron were carried out by precipitating the iron with base (NaOH, NH_4OH or urea), washing the precipitate and then adding the desired amount of silver containing a trace of silver -110 at the predetermined pH. The amount of silver adsorbed was determined by measuring the change in the silver concentration of the solution using radiotracer techniques. After equilibrium was established the silver concentration of the washed precipitate was also measured.

The coprecipitation tests with iron were carried out by precipitating the iron with base from mixtures of iron and silver solutions.

For example: the adsorption values were obtained as follows: 100 ml of 1410 ppm Fe^{3+} solution was titrated with dilute base with vigorous stirring. The resulting precipitate was washed 3 times with 60 ml hot 1% $NaNO_3$ adjusted to the pH at which the experiment was to be carried out. The $NaNO_3$ was used to prevent the peptization of the precipitate at the lower pH values. The precipitate was then mixed with pH adjusted $AgNO_3$ solution containing 2g $NaNO_3$ and sufficient water to make a total volume of 200 ml. The resulting mixture was stirred intermittently. All pH adjustments were made with NaOH, NH_4OH or HNO_3. The Ag^+ concentration changes were measured periodically by centrifuging a 30 ml aliquot and measuring the counting rate of two 5 ml aliquots of the clear solution. These aliquots were then returned to the mixture.

Homogeneous precipitates prepared by boiling the iron solution with urea as described by Willard and Tang (1937), were treated in the same way as precipitates prepared by titration in subsequent adsorption tests.

The adsorption of silver ion on freshly prepared manganese dioxide was studied by adding a known amount of silver to a washed batch of precipitate and measuring the change in tracer concentration of the solution with time, keeping volume and pH constant. Coprecipitation tests were carried out by precipitating MnO_2 in the presence of the silver ion.

Batches of hydrous manganese dioxide were prepared by two different methods. One method described by Sarkar and Dhar (1922), can be represented by the following reaction:

$$3Mn(NO_3)_2 + 2KMnO_4 + 2H_2O = 5MnO_2 + 2KNO_3 + 4HNO_3$$

In our work standardized $KMnO_4$ was added to a solution of $Mn(NO_3)_2$ containing 1% $NaNO_3$ with vigorous stirring until the desired amount of MnO_2 was precipitated, i.e. 2.0×10^{-4} moles per batch. Yields averaging 96% were obtained in this way. The second method employed H_2O_2 as follows:

$$2KMnO_4 + H_2O_2 = 2MnO_2 + 2KOH + 2O_2$$

In this case yields averaged 82%. To obtain 2.0×10^{-4} moles of MnO_2, excess H_2O_2 was added to 20 ml of 0.010 molar $KMnO_4$ solution containing 1% $NaNO_3$. When yield corrections were applied to silver adsorption data obtained with precipitates prepared by the two methods no significant differences were observed, even though the volume of MnO_2 by the first method for 2.0×10^{-4} moles was 1.0 ml compared to 1.8 ml using the second method. Hydrous oxides of iron and manganese were prepared in the following manner: aliquots of ferric and manganese nitrate solutions were mixed and titrated with potassium permanganate solution, keeping the pH of the mixture near 3. Reproduceable samples of these mixtures were more difficult to prepare than the pure oxides; small changes in timing or stirring rate resulted in significant changes in colour of the precipitate and amount of silver adsorbed. In general the colour of the final product was dark brown to black, with the lighter coloured precipitates adsorbing less silver. The washed mixed oxides were then mixed with silver solution and silver adsorption studied as in the case of the pure oxides. The peroxide method gave much poorer results in the case of iron-manganese mixtures, and hence was not used for subsequent adsorption studies.

The adsorption tests of silver by natural hydrous oxides were first carried out by adding a known amount of silver to an aliquot of the natural solution containing 2 to 5 ml of precipitate. However, due to the presence of ions such as Cl^-, which form insoluble silver salts or at very high concentrations-soluble silver complexes, these tests were meaningless. Somewhat more meaningful results were obtained using washed precipitates. Subsequent tests were therefore carried out on washed precipitates keeping the pH of the artificial solutions the same as that of the natural solutions, and adding a known amount of silver. After equilibrium was established, i.e., the Ag concentration no longer changed appreciably with time, the precipitates were dissolved and the amount of iron and manganese determined by standard colorimetric methods. The concentration of ions in the natural solutions and the major constituents of the precipitates are given in Tables 3 and 4. Dissolved ions were determined by standard water laboratory methods and the composition of the precipitates was determined spectrographically.

Solutions

The silver solutions were prepared by accurate dilution of a 0.02M $AgNO_3$ stock solution prepared from pure $AgNO_3$ crystals. To minimize adsorption on walls of storage bottles the pH of the diluted solution was kept below 2. A convenient quantity approximately 20 microcuries of Ag-110 m was added to one litre of solution to measure subsequent silver concentration changes. The secondary stock solutions contained 216, 21.6, 2.16, 0.216 and 0.022 ppm Ag^+.

Reagent grade $Fe(NO_3)_3$. $9H_2O$ was dissolved in water and kept at a pH 1 with HNO_3 to prevent the formation fo colloidal iron oxide. The stock solution was standardized gravimetrically and colorimetrically. Aliquots of this stock were then diluted to give 1410 ppm Fe^{3+} secondary stock solution.

Standard 0.01M solutions of $KMnO_4$ and $Mn(NO_3)_2$ were prepared by accurately diluting 0.1M $KMnO_4$ and 0.1M $Mn(NO_3)_2$ solution which were standardized colorimetrically against standard manganese solutions prepared from the pure metal. The 0.1M solutions were prepared by dissolving crystalline $KMnO_4$ and by diluting a 50% solution of $Mn(NO_3)_2$.

Instruments

All pH measurements were made with a model 22 Radiometer pH meter. To avoid chloride contamination of experimental solutions the $KC\ell$ in the calomel salt bridge was replaced by KNO_3. Silver concentration changes were measured with a Harshaw 3-inch well type NaI $(T\ell)$ crystal and a single channel pulse height analyzer Victoreen model 851A. The instrument was set to record the 0.656 Mev gamma ray of Ag-110 m.

Errors

Because of the large silver concentration range, cross-contamination was found to be one of the most troublesome factors. To achieve an average reproduceability of ± 5 per cent, for studies of silver and hydrous ferric oxide several experiments had to be carried out with a set of laboratory ware to condition all the pieces to a particular silver concentration. Counting errors and volume measurement errors were easily kept below $\pm 1\%$ in most cases. The 5 ml aliquots could be measured accurately with pipettes. By adding sufficient tracer to the solutions, the 10,000 counts required to give an error of $\pm 1\%$ (95% confidence limit) were easily accumulated in all but a few cases where adsorption exceeded 98%. With hydrous ferric oxide, steps such as the use of large solution volume to apparatus surface area ratios and magnetic stirring bars sealed in glass rather than teflon, were found to be essential to avoid excessive loss of silver at the lower silver concentrations.

Because hydrous manganese dioxide adsorbed much larger quantities of silver per unit weight than hydrous ferric oxide, higher silver concentrations were used and hence loss of silver on glass ware became negligible. However, loss of MnO_2 due to sticking of the finely divided solid on the wall of beakers was troublesome. With care average reproduceability with pure hydrous MnO_2 could be kept within $\pm 5\%$. With mixtures of hydrous MnO_2 and Fe_2O_3 reproduceability was poorer. Adsorption of silver in this case could be correlated roughly with the colour of the mixture, the darker the mixture the greater the adsorption. The colour of the precipitate mixture was somewhat dependent on the rate at which reagents were mixed. Several explanations for this behaviour could be offered but since none were tested they are not described.

From the observations made during this study the degree of homogeneity of the precipitates was found to be the deciding factor in determining reproduceability.

RESULTS AND DISCUSSION

Adsorption on hydrous ferric oxide

As is evident from Figure 1, the adsorption of Ag^+ by freshly prepared hydrous ferric oxides from very dilute solution can be represented by the well known Freundlich adsorption equation

$$X/M = k\, C^{1/n}$$

where X/M = ratio of the amounts of silver and iron in the precipitate at the equilibrium silver concentration C; k and n are constants which give the intercept and slope of the straight line of a log-log plot of the above equation. Experience has shown that it applies to surfaces of high-energy heterogeneity of adsorption sites. Oxides are typical of these. It is also evident that the hydrogen ion concentration greatly influences the amount of silver adsorbed. Competition between silver and hydrogen ions is evident.

Figure 1A represents solution measurements and Figure 1B washed precipitate measurements. Extensive washing did not change X/M appreciably at the lower concentration range even though 10 to 20 per cent of the silver and iron were lost during washing. At the high equilibrium concentrations but low pH relatively more silver was washed out than iron, i.e., X/M decreased somewhat. Washing probably peptizes the oxide, i.e., fragments the oxide down to near colloidal size. The constant X/M implies that the Ag^+ is evenly dispersed throughout the oxide. This constant silver-iron correspondence also suggests that the adsorption forces which bind silver to hydrous iron oxide are nearly as strong as those binding the hydrated iron oxide molecules to each other. Silver ferrites $(AgFeO_2)_3$ are known to form only under extreme conditions such as boiling in NaOH (Krause and Pilawski, 1931).

X/M values obtained from measurements with precipitates prepared with urea are generally about 2 to 4 times lower than those from NaOH precipitations. Since the amount of iron was kept constant in all experiments, it follows that about 2 to 4 times less silver is adsorbed by these precipitates. This could be because the precipitates prepared with urea were much denser than those from NaOH, the average volume of 20 centrifuged precipitates being 3.6 ml compared to 5.4 ml of 50 NaOH prepared precipitates. Urea hydrolyzes slowly to produce OH^-, yielding more stable oxide surfaces and therefore of lower specific area, i.e., larger crystallites. High temperatures speed up the "aging" (a dehydration process which removes -OH sites) of gels which eventually results in the transformation from the amorphous to the crystalline state. However, X-ray analysis* of two preparations, one by each method, did not reveal lines in either precipitate.

To prevent extensive peptization of iron precipitates, especially at the lower pH values, all experiments were carried out in 1 per cent $NaNO_3$. The values represented by tailed points in Figure 1 (adsorption isotherm pH = 6) were obtained without $NaNO_3$ and show that the electrolyte does not

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*Carried out by R.N. Delabio, Geological Survey of Canada.
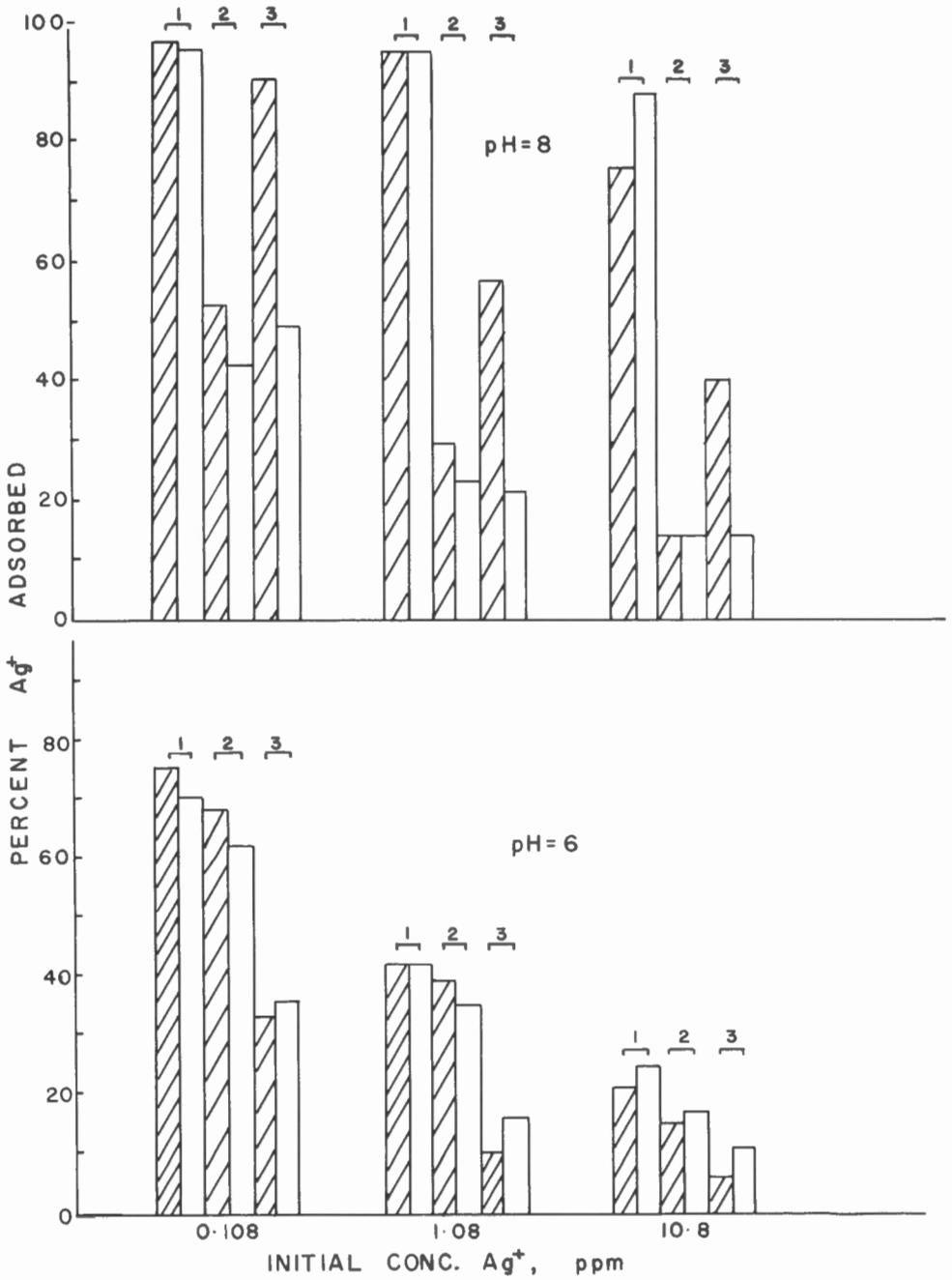
Figure 2. Histogram comparing adsorption and coprecipitation values at selected silver concentrations. Lined bars represents adsorption clear bars coprecipitation values. 1, 2 and 3 refer to NaOH, NH_4OH and urea prepared precipitates respectively (2.53×10^{-3} moles Fe^{3+} equivalent).
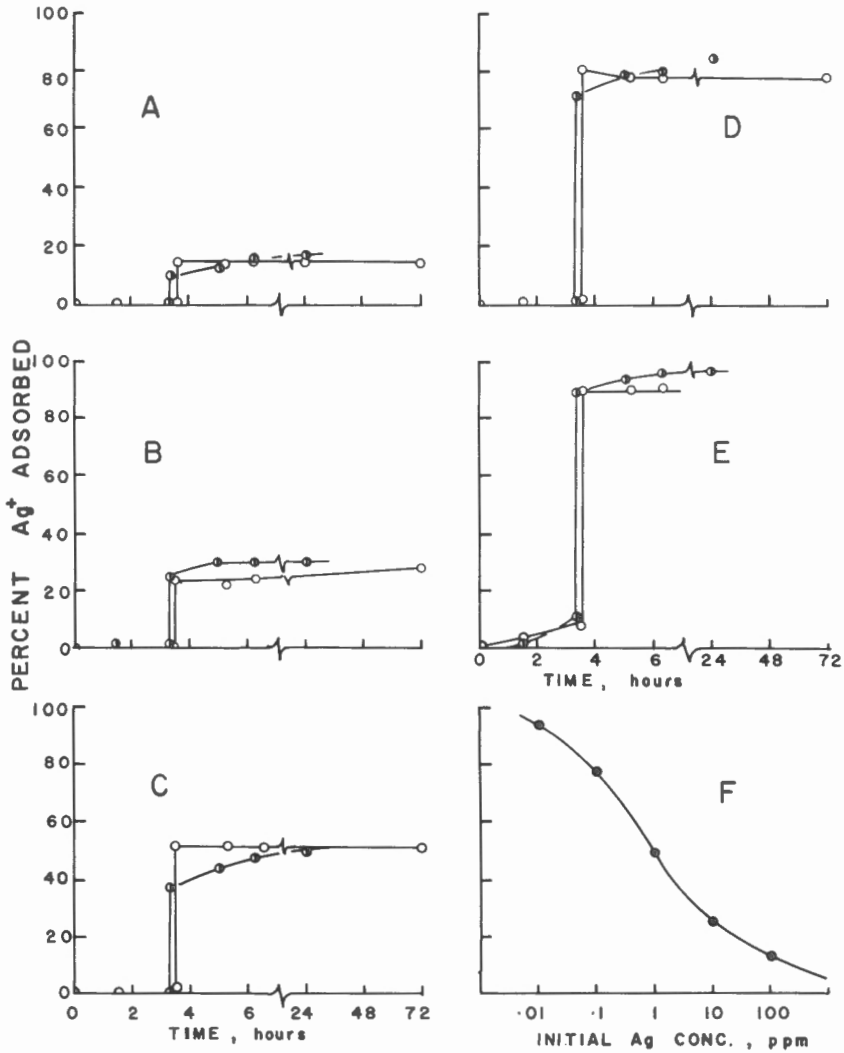
Figure 3. Details of 2°C and 50°C adsorption isotherms at a constant pH of 6.0. Step in functions A to E occurs at instant of mixing freshly prepared hydrous ferric oxide precipitate (2.53 x 10^{-3} moles Fe^{3+} equivalent) with 200 ml AgNO$_3$ soln.
0 = 2°C isotherm; 0 = 50°C isotherm.
Initial silver concentrations, in ppm: A = 108; B = 10.8; C = 1.08; D = 0.108; E = 0.011. F - average of the two isotherms about 3 hrs. after mixing precipitate with soln.
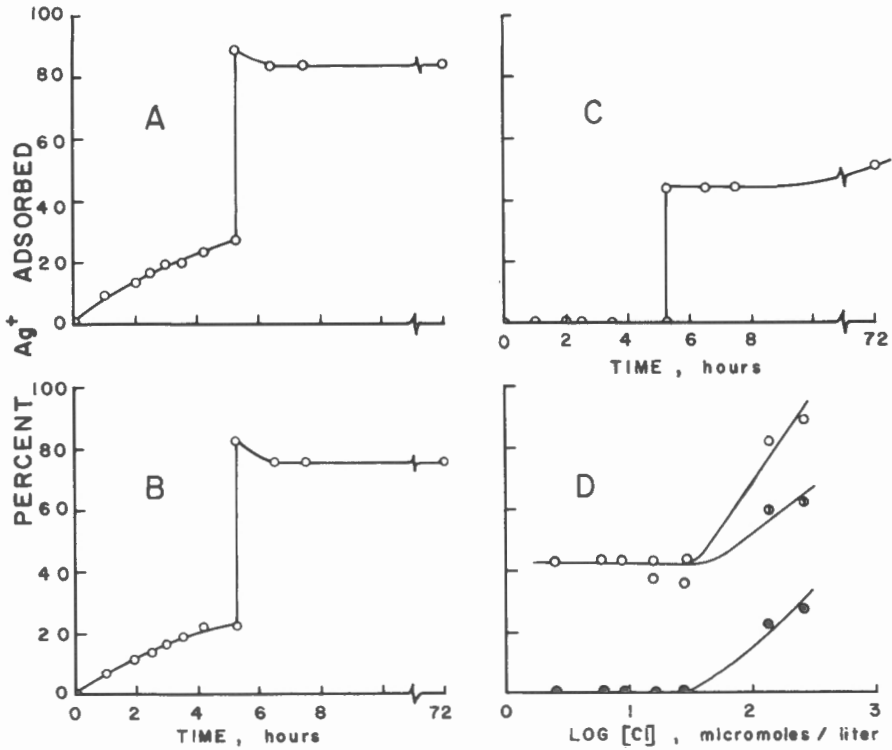
Figure 4. Effect of chloride ions on adsorption of silver. Step in functions
A to C occurs at instant of mixing freshly prepared hydrous ferric
oxide precipitate (2.53×10^{-3} moles Fe^{3+} equivalent) with 200 ml
of 1.08 ppm $AgNO_3$ soln. at a pH of 6.0. Initial chloride ion conc.
in micromoles/litre; A = 255; B = 136; C = 29; D - summary of all
chloride tests; lowest chloride ion conc. was added with reagents
(Calc. from impurity data given on reagent bottle labels).
0 = total Ag^+ removed from solution; 0 - Ag^+ removed by beaker;
as AgCl; 0 - Ag^+ removed by precipitate.

interfere with the adsorption of silver. The lower X/M values of this iso-
therm in Figure 1B coincide with excessive loss (~30%) of precipitate during
washing.

That adsorption and coprecipitation results are nearly identical can
be seen by examining the results shown in Figure 2. Given sufficient time
the amount of silver coprecipitated approaches the amount adsorbed. Appre-
ciable complexing of silver by ammonia starts only at a pH above 6. This
explains the difference shown in Figure 2, between the NaOH and NH_4OH pre-
pared precipitates at a pH of 8. The difference between the adsorption and
coprecipitation values of the precipitates from urea at a pH of 8 is due to the
fact that the adsorption values were obtained from washed precipitates and
solutions containing no ammonia (i.e. NaOH was used to adjust the pH of the
solutions).

Figure 3 illustrates details of the 2°C and 50°C experiments at a pH of 6. It is obvious from these graphs that temperature plays an insignificant role in the adsorption process under investigation. The graphs also illustrate the speed with which silver is adsorbed; the step in functions A to E represents measurements taken 5 minutes apart.

Because ions forming insoluble silver salts can influence the adsorption of Ag^+ appreciably, chloride tests were carried out to determine what role Cl^- ions would play in the adsorption tests described here. These are shown in Figure 4. Only after increasing the Cl^- concentration by a factor of 10 from that added initially with the various salts (as calculated from impurity labels on reagent bottles) is an increase in the adsorption of Ag^+ observed, probably due to plating out of $AgCl$.

Adsorption on hydrous manganese dioxide

As noted in the introduction, considerable work has been carried out on the adsorption of ions on manganese dioxide and thus only a few experiments were carried out to obtain a measure of the amount of silver that is adsorbed per unit weight of hydrous manganese dioxide. The results of these experiments are shown in Figure 5A. The dependence of adsorption on pH is illustrated in Figure 5B. From these results and the results for hydrous ferric oxide it can be seen that manganese is a much better adsorber of silver than is iron. In fact, at a pH of about 6.5 to 7.0 and a silver equilibrium concentration of 5 ppm, one ml of manganese (as the manganese dioxide) will adsorb roughly 25-45 times as much silver as will one ml of iron, and one gram of manganese about 130 times as much as one gram of iron.

As was the case with iron, there is no appreciable difference between adsorption and coprecipitation results. Neither do the silver adsorption results depend on the mode of precipitation of hydrous manganese dioxide, i.e., $Mn(NO_3)_2$ versus H_2O_2 method.

The effect of temperature on the amount of silver adsorbed was negligible. The rate of adsorption was relatively fast; there was very little change in the amount of silver adsorbed after 2 to 5 minutes of stirring of mixtures.

Adsorption on mixtures of hydrous oxides of iron and manganese

In nature mixtures of iron and manganese oxides are much more common than the pure oxides. An attempt was therefore made to simulate natural conditions in the preparation of mixtures of hydrous oxides and to study the adsorption of silver on them. The first attempts involved the titration of mixtures of silver, iron-III and manganese-II with NaOH in the presence of H_2O_2. Under these conditions the precipitate would not form until a pH of about 6 even though a period of as much as three days was allowed between pH changes. The results indicated however, that the presence of Mn in an Fe solution causes the iron to be precipitated at a faster rate than if the iron solution contained no manganese. Also the iron manganese mixtures caused coprecipitation of silver to begin at lower pH values than if the
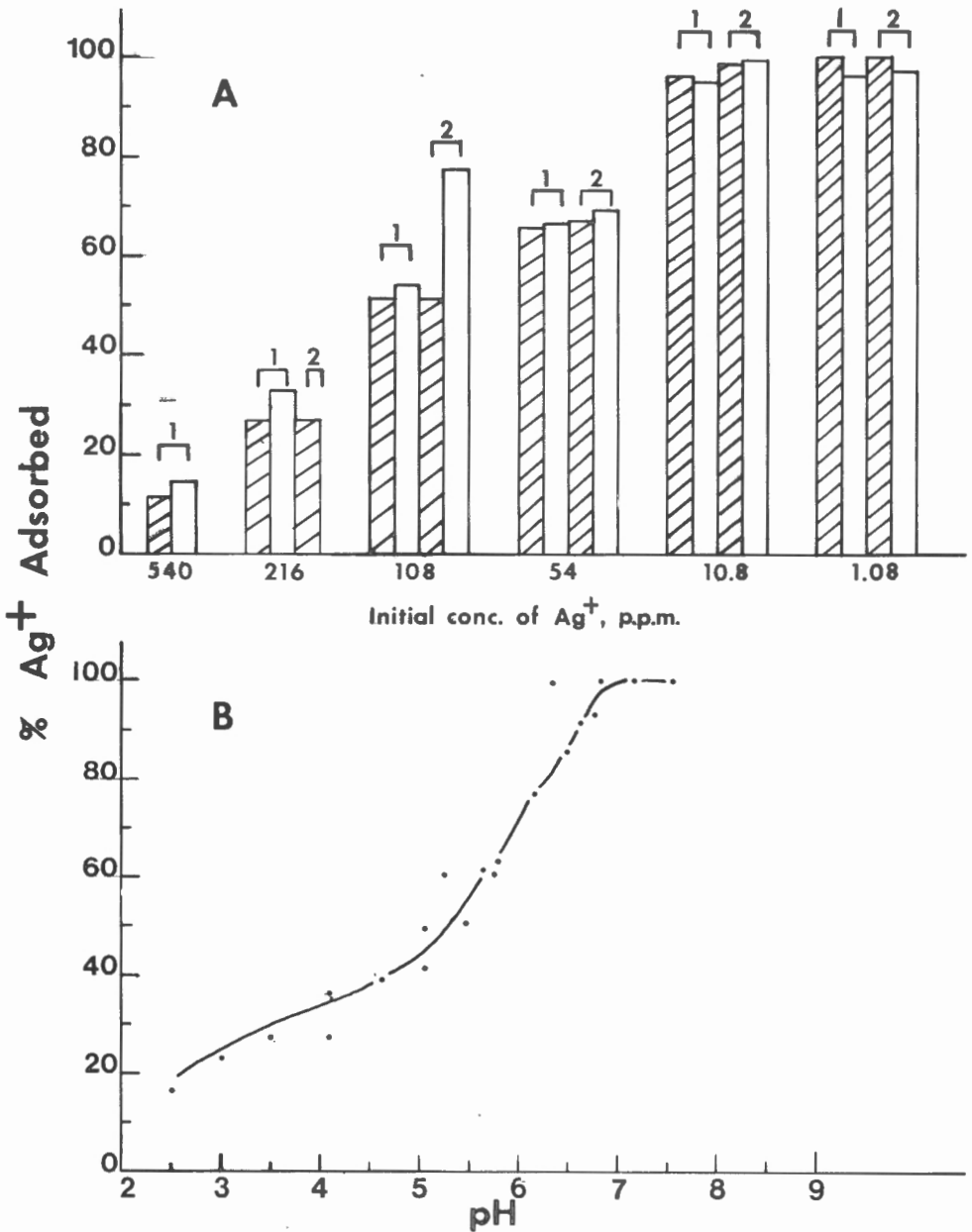
Figure 5. Adsorption and coprecipitation of silver on freshly prepared
hydrous manganese dioxide.
  A. Per cent silver adsorbed or coprecipitated as a function of
      initial silver concentration in a total volume of 100 ml and a
      pH of 6.0; amount of oxide = 10.9 mg Mn equivalent. 1 = oxide
      prepared by the $Mn(NO_3)_2$ method; 2 = oxide prepared by the
      H_2O_2 method. Cross-hatched columns refer to adsorption
      tests and clear columns to coprecipitation tests.
  B. Adsorption of silver as a function of pH.
      Initial silver concentration = 50 ppm in a total volume of 100 ml.
      Amount of hydrous oxide per batch = 10.9 mg Mn equivalent.

solution contained only one of the metal ions. This is probably a consequence of the manganese acting as coagulating agent which caused the colloid or iron hydroxide to be removed at lower pH values. Several coprecipitation results are listed in Table 1.

Because the results obtained by the titration method were difficult to reproduce a number of tests were carried out in which the precipitate was prepared first and then a known amount of silver was added to the precipitate. The results of these tests are summarized in Table 1. As is evident the amount of iron has very little effect on the amount of silver that is adsorbed, confirming the much greater adsorption capacity of manganese hydroxide compared to that of iron hydroxide.

Adsorption on natural hydrous oxides

During the 1967 field season 17 samples of natural hydrous oxides in their native solutions, 2 from the Dawson Settlement area in New Brunswick, 3 from Walton, Nova Scotia, and 12 from Cobalt, Ontario, were analyzed for the common constituents and studied for their silver adsorption properties. The type, location and silver concentration of these samples is given in Table 2. Chemical analyses of the clear solutions and spectrographic analyses of the dry sediments are listed in Tables 3 and 4, respectively. Results of silver adsorption tests are summarized in Table 5.

The samples come from silver mining areas and therefore were analyzed for silver using a mild acid leach in order to ascertain whether the original silver adsorbed on the samples could distort the silver adsorption test results obtained in the laboratory using a silver tracer. Calculations, using the silver concentrations from Table 2, show that the amount of silver present originally comprised at most only about one tenth the amount added for the test.

The discrepancy in the pH values between Tables 2 and 5 are probably due to loss of carbon dioxide on standing; results of Table 5 were obtained in September 1967 and those of Table 2 in April 1968. It may be of interest to note a few element associations between the solid and liquid phase of the samples, e.g. SiO_2 (solid)-SiO_2 (solution); the association of CaO (solid)-HCO_3^- (solution) and Ca (solution)-SO_4 (solution) implies that the calcium is precipitated as the $CaCO_3$ but has a common origin with the sulphate ion. The association of aluminum and titanium with silicon in the precipitates is interesting but not really surprising. All elements belong to the refractory group; their main chemical similarity is their inertness when bound to 0. M-O bond strengths for Al, Ti, Si are all very high. They present what are virtually oxygen surfaces. The similarity of alumina and silica is evident from their common occurrence in natural silicates such as micas and feldspars, and titanium-4, the most stable natural form of titanium, is usually bound covalently and hence its chemical properties become similar to those of silica.

The results of adsorption tests listed in Table 5 were obtained as follows: the precipitate and solution of a sample were well shaken, an aliquot of this mixture was then centrifuged, the precipitate washed in a 1 per cent $NaNO_3$ solution, and a known volume of the precipitate (1 to 5 ml) was then mixed with a silver solution of known concentration and a pH equal to that of the original solution. The amount of silver adsorbed per ml of precipitate

using the original solution was almost twice that adsorbed on the washed precipitate but only when the chloride and bicarbonate concentration was sufficiently low that silver would not precipitate. In the latter case large amounts of silver would adsorb and precipitate in accordance with solubility and adsorption laws. Tests with clear solutions showed that when the solution was supersaturated but the silver concentration $\leq 10^{-3}M$ and the chloride to silver ratio 10 or greater, silver would complex and not precipitate. When the above conditions were not met silver would precipitate, the amount being determined by the solubility of silver chloride and silver carbonate. Material balance and ion product calculations showed that for most samples appreciable dissociation of bicarbonate was required to account for the precipitated silver. In the presence of sample precipitate silver would come down even if conditions in the solution were right for the formation of the silver chloride complex. The reason for using millilitres of precipitate rather than the conventional grams was because it was felt that drying might destroy or change the adsorption capacity of the original precipitates. For the iron-rich precipitates the weight of 1 ml would reach several hundred mg. It may be of interest to note that 25 per cent by weight of the air-dried precipitate was organic or volatile and could be driven off over a bunsen burner. Also, about 80 per cent by volume of the precipitates was soluble in nitric acid. Residues from nitric acid leaches consisted mainly of silica and sand. This residue adsorbed very little silver compared to the original precipitate.

Under conditions of silver saturation (Test 1, Table 5), the adsorption tests show that an increase of iron and manganese increases the amount of silver adsorbed, however other factors, probably the presence of ions which form insoluble salts with silver, greatly enhance the adsorption capacity of the natural precipitates. For example; at a pH of 6.5 to 7.0 and an equilibrium silver concentration of 5 ppm a 1 ml laboratory sample of pure hydrous oxide of iron contains 24 mg of iron and will adsorb about 0.1 mg of silver; a 1 ml laboratory sample of hydrous manganese dioxide contains about 10 mg of manganese and will adsorb 2.5 to 4.5 mg of silver; but 1 ml of the natural precipitate containing 0 to 40 mg of iron and only traces of manganese adsorbs about 10 mg of silver (see samples 67/160001, -2, -3, and 67/170007, -8, -9, Test 2, Table 5). Furthermore, the dependence on the amount of iron is very slight. The results of Test 1 also show that several natural precipitates contain much more iron or manganese per ml than the laboratory prepared precipitates do. This is probably due to the fact that the natural precipitates form much more slowly in very dilute solutions. As was noted in the discussion on the preparation of ferric oxides that the precipitates formed by homogeneous precipitation (boiling with urea) resulted in a noticeably denser precipitate.

The results of the first five samples of Test 2 were obtained with a 5 ml aliquot of washed precipitate in 100 ml of 0.01 ppm solution of silver. In view of the low equilibrium silver concentration and the large adsorption capacity of the precipitate one can readily understand why natural waters, as a rule, contain silver concentrations below a part per billion. However, solutions containing large amounts of chloride and/or sulphate will carry several ppb of silver (see samples W-67-E-10 and 67-D-10, Table 2).

CONCLUSION

The adsorption of silver by pure hydrous oxides of iron and manganese in very dilute solutions can be represented by Freundlich adsorption isotherms, is strongly dependent on pH, but practically independent of temperature in the range 0° to 50°C. For example, an increase in the hydrogen ion concentration of 10^4 decreases the adsorption of silver by 10^2.

Adsorption and coprecipitation tests show that under identical environments and equilibrium conditions, identical amounts of silver are incorporated by the hydrous oxides of iron and manganese.

The high speed with which adsorption takes place and the pH dependence strongly suggest H+ and Ag^+ ion exchange.

Natural hydrous oxide precipitates adsorb much larger amounts of silver than do laboratory preparations under similar conditions of pH and equilibrium silver concentrations due to the presence of ions which form insoluble compounds with silver.

Igneous rocks have an average iron to silver ratio of 500,000 to 1 and a manganese ratio of 10,000 to 1. Either ratio is much larger than any of the ratios used in the experiments in this study. Assuming indiscriminate leaching of the 3 elements in nature, subsequent precipitation of iron and manganese would result in virtual removal of silver from solution. Hence natural waters near the neutral point cannot be expected to carry silver in solution in easily detectable quantities. Limonite and wad on the other hand, can be expected to contain silver if the ion was present in the solution from which the limonite precipitated.

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APPENDIX

Table 1

Grams Ag per gram of Mn (x/m) as a function of iron. Initial Ag+
concentration = 108 ppm. Initial Mn^{++} concentration = 109 ppm;
pH = 6.0. Total volume of solution = 100 ml.

grams of Fe added	5450×10^{-4}	706×10^{-4}	109×10^{-4}	15.57×10^{-4}	8.0×10^{-4}
x/m by adsorption	0.550	0.317	0.471	0.411	0.485
by coprecipitation	0.590	0.367	0.485	0.515	0.485

Table 2.   Location, type and silver content of natural hydrous oxides

Precipitate		Color of dry precip.	Ag conc.**	
Number*	Type and Location		Precip., ppm	Clear sol'n. ppb
Mn Dawson Sett.	Spring, Dawson Settlement, N.B.	black	< 0.3	0.5
Fe Dawson Sett.	Spring, Dawson Settlement, N.B.	brown	0.4	< 0.3
W-67-D-10	Brine, Magnet Cove, Barium Corp., Walton, N.S.	red-brown	< 0.3	8.1
W-67-E-10	Brine, Magnet Cove, Barium Corp., Walton, N.S.	red-brown	< 0.3	5.5
W-67-C-12	Gypsum and anhydrite leach, Walton, N.S.	l. brown	< 0.3	1.3
67/160001	Spring, east of Cobalt Lake	grey	28.0	3.5
67/160002	Spring, east of Cobalt Lake	d. grey	40.0	0.7
67/160003	Spring near Little Silver Vein	l. grey	4.3	0.3
67/170001	Fault zone, Langis No. 3 shaft, 355 level	brown	1.8	0.2
67/170002	Fault zone, Langis No. 3 shaft, 425 level	red-brown	2.4	0.4
67/170003	D.D.H. 297, Cleopatra vein, Hiho.	grey	23.0	0.2
67/170004	D.D.H. and fault, Silverfield, 608 level	brown	37.0	0.3
67/170005	Fracture zone, Deer Horn, 800 level	d. brown	21.0	2.6
67/170006	D.D.H.-776, Deer Horn Mine	brown	3.2	< 0.6
67/170007	D.D.H.-349, Deer Horn, 525 level	d. brown	6.0	< 0.3
67/170008	Fracture zone, 407 shaft, Agnico Mine	brown	1.9	0.3
67/170009	Fracture zone, 407 shaft, Agnico Mine	brown	3.0	< 0.3

*   The 1st five samples were collected by R.W. Boyle and the remaining
     samples by A. Dass, G.S.C., Ottawa.

** Analyses were carried out by G. Gauthier, G.S.C., Ottawa.

Table 3. Results of analysis of water samples*

Sample Number	pH	Ca	Mg	Na	K	CO$_3$	HCO$_3$	SO$_4$	Cl	F	PO$_4$	NO$_3$	SiO$_2$
								Concentration of ions, ppm					
1. Mn Dawson Settlement	5.2	175.0	34.0	5.7	10.1	0.0	0.4	757.0	3.0	-	0.13	0.18	17.0
2. Fe Dawson Settlement	7.1	27.3	1.4	3.5	2.2	0.0	70.0	25.9	2.4	0.13	0.21	0.06	11.9
3. W-67-D-10	6.9	936.0	115.0	8,780.0	105.0	0.0	105.0	2,158.0	16,000.0	-	0.02	5.90	2.9
4. W-67-E-10	6.9	912.0	125.0	6,690.0	97.0	0.0	97.8	2,250.0	13,200.0	-	0.02	6.70	2.9
5. W-67-C-12	7.0	507.0	22.5	16.4	2.5	0.0	65.3	1,260.0	8.2	-	0.04	1.70	7.0
6. 67/160001	7.6	94.4	136.0	2.0	8.8	0.0	1,193.0	1.9	2.5	-	1.70	<0.05	15.9
7. 67/160002	7.1	102.0	32.9	1.7	6.0	0.0	590.0	5.2	1.4	-	0.87	0.07	21.0
8. 67/160003	7.4	106.0	45.0	2.8	4.3	0.0	580.0	8.1	1.5	-	0.19	9.00	12.5
9. 67/170001	8.4	91.3	34.3	69.3	3.5	3.6	396.0	57.0	92.5	-	0.12	0.90	11.5
10. 67/170002	7.9	67.1	30.9	61.0	3.8	0.0	330.0	59.7	65.5	-	0.07	4.30	5.4
11. 67/170003	7.6	50.2	16.2	15.4	1.4	0.0	239.0	22.6	3.9	-	0.35	1.70	14.0
12. 67/170004	7.5	115.0	34.7	9.6	1.8	0.0	305.0	195.0	2.0	0.13	0.19	0.04	7.7
13. 67/170005	7.2	528.0	133.0	207.0	5.9	0.0	90.4	40.3	1,800.0	-	0.82	2.50	13.2
14. 67/170006	7.2	481.0	58.0	288.0	5.4	0.0	238.0	87.8	1,340.0	0.65	0.21	0.04	21.3
15. 67/170007	7.8	240.0	38.0	210.0	5.0	0.0	202.0	28.9	780.0	-	0.15	<0.05	13.5
16. 67/170008	7.3	91.4	35.2	11.3	2.7	0.0	393.0	55.8	14.5	-	8.70	0.24	20.0
17. 67/170009	7.5	64.4	24.1	23.4	3.0	0.0	266.0	55.9	27.0	-	5.80	0.62	18.6

* Analyses were carried out by J. P. Lively, Inland Waters Branch, Department Energy, Mines and Resources, Ottawa.

Table 4. Results of spectrographic analysis of dry sediment samples*

Sample Number	MnO	MgO	Al_2O_3	SiO_2	Fe_2O_3	CaO	TiO_2
Mn Dawson Settlement	> .6	0.22	2.81	2.0	21.0	2.45	.03
Fe Dawson Settlement	> .6	0.2	0.2	8.3	> 20.0	2.6	< .03
W-67-D-10	.11	0.2	0.3	4.4	> 20.0	1.4	< .03
W-67-E-10	.12	< 0.1	< 0.1	4.9	> 20.0	1.9	< .03
W-67-C-12	.07	0.9	14.0	47.5	19.2	1.2	0.50
67/160001	.01	1.7	3.8	15.9	1.4	> 30.0	0.06
67/160002	.08	1.2	7.2	36.0	6.1	1.7	0.25
67/160003	.03	0.7	2.0	7.4	0.8	> 30.0	0.03
67/170001	> .6	0.6	0.4	10.5	> 20.0	4.6	< .03
67/170002	.09	0.8	2.4	18.3	> 20.0	4.1	0.03
67/170003	.29	5.9	11.6	36.6	> 20.0	3.0	0.42
67/170004	> .6	2.1	4.3	16.2	> 20.0	> 10.0	0.17
67/170005	.05	2.0	4.7	16.5	> 20.0	4.6	0.04
67/170006	.08	0.7	1.6	25.5	> 20.0	2.4	0.03
67/170007	.15	·1.3	2.8	23.2	> 20.0	2.0	0.05
67/170008	> .6	2.9	2.9	22.5	> 20.0	9.1	0.14
67/170009	.22	1.1	2.4	12.8	> 20.0	> 10.0	0.04

Concentration, %

* Analyses were carried out by R. Horton, Geological Survey of Canada, Department of Energy, Mines and Resources, Ottawa.

Table 5. Results of adsorption tests of silver on washed natural precipitates of hydrous oxides

| Sample Number | pH | Test 1. | | | | Test 2. | | | |
| | | Equilibrium Ag$^+$ conc., ppm | Element conc. g/ml precipitate x 10^{+4} | | | Equilibrium Ag$^+$ conc., ppm | Element conc. g/ml precipitate x 10^{+4} | | |
			Ag	Fe	Mn		Ag	Fe	Mn
Mn Dawson Settlement	6.35	756	324	356	354	.00036	.00212	650	308
Fe Dawson Settlement	6.57	972	108	503	65	.00035	.00212	720	109
W-67-D-10	6.07	972	108	1260	1	.00032	.00213	1110	2
W-67-E-10	6.80	842	240	2140	2	.00019	.00216	1900	2
W-67-C-12	6.35	1030	50	382	1	.00007	.00217	450	1
67/160001	6.86	935	95	3	0	5.4	102.	24	0
67/160002	6.71	980	65	2	0	9.7	99.	1	0
67/160003	7.00	875	127	3	0	5.4	102.	1	0
67/170001	7.27	810	135	361	11				
67/170002	7.34	875	194	500	0				
67/170003	6.90	835	206	334	2				
67/170004	7.35	675	192	198	7				
67/170005	7.00	548	253	405	0				
67/170006	6.50	652	194	232	0				
67/170007	7.04	880	134	85	0	5.4	102.	104	0
67/170008	7.61	622	306	228	5	3.2	105.	180	3
67/170009	7.44	454	417	200	1	6.5	102.	412	2