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OHN D. HEM

EMISTRY OF MANGANESE IN NATURAL WATER

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By John D. Hem

ABSTRACT

Manganese is essential for plant growth and some aquatic species contain onsiderable amounts. Manganese oxide deposits, generally mixed with iron xide, occur in streambeds and in lakes in some areas. Manganese oxide is n important constituent of desert varnish.

Feldspathic sand removes manganese from dilute solutions by cation exhange, and above pH 7.0 the sand acts as a catalyst in the oxidation of mangaous ions by aerated water. The catalytic effect was strongest in sand whose xchange positions had been saturated with manganese and which had been horoughly dried. Manganese was a little more strongly absorbed than calcium.

Manganese oxide coprecipitated with ferric hydroxide in aerated solutions bove pH 6.5. Mixed deposits of iron and manganese oxides can form in fresh water environments at a pH and redox potential where manganese oxide would not be precipitated alone if the ferrous iron activity in solution is maintained at a very low value.

NATURAL OCCURRENCE OF MANGANESE

Manganese oxides may accumulate on the surfaces of rocks in the beds of certain lakes and streams, and are a major part of the dark surface coating known as desert varnish which occurs on the surfaces of rocks in some arid regions. Manganese also is a widespread though usually rather minor constituent of soils. Whether manganese is present in soils as oxide, as a constituent of silicate or other minerals, or is held by adsorption at the surfaces of clay minerals probably depends on numerous factors that vary from one soil to another. Manganese oxide accumulations below the surface of rice-paddy soils are mentioned by Kawaguchi and Matsuo (1955) and have been observed and studied in many places by other soil scientists. Nodules of manganese dioxide admixed with iron oxide occur on the floors of ocean basins.

These accumulations of manganese oxide are of interest in the chemistry of manganese in water because they represent deposition of a substance which was once carried in solution. The purpose of this discussion is to identify some of the more likely chemical facto which caused deposition to take place. Some conclusions as to wh the controlling factors maybe have been drawn from published liter ture and others have been based upon experiments performed by th writer and his coworkers.

MANGANESE IN SOIL AND PLANTS

Manganese is an essential minor element to plant growth. Becaus of its agricultural importance, a considerable amount of informatio on the manganese content of soils exists. Shawarbi (1952, p. 140 observed that soils in the United States commonly contain from 0.00 to somewhat over 1 percent manganese, but that some tropical soi contain as much as 15 percent. Thorne and Peterson (1954, p. 260 noted that manganese deficiency most often occurs in soils at neutr or slightly alkaline pH.

Earlier study by the writer (Hem, 1963) suggests that manganes oxides are appreciably soluble in aerated water of pH as high 9.0. This solubility suggests that manganese might be readily leache from many soils. Iron is sometimes not available to plants when th soil pH becomes too high. Manganese, however, would remain avai able well above the pH where iron deficiencies would begin to occu

Manganese is known to be adsorbed strongly in cation-exchan processes, but little information on the strength of adsorption manganese compared with that of other ions seems to be availab Because the Mn^{+2} ion is smaller than the calcium ion, however, an because both are divalent, manganese probably is held more strongl than calcium, and is therefore somewhat enriched in the adsorbe phase and impoverished in the solution phase.

The role of manganese in plant metabolism is not fully understoo Tanner and others (1960) reported a chlorophyll synthesis in whic manganese is involved, evidently in a cyclic series of oxidations an reductions. Whether the main function of the element in plants is re lated to this synthesis or to other processes, the manganese conten of plants is generally appreciable. Erkarna (1947) reported a con tent of 13 to 1,280 mg of manganese per kilogram of plant leaves, pre sumably on a dry basis. Data of earlier investigators are in approxi mate agreement, and seem to suggest that the submerged fresh-wate plants are the highest in manganese content of the types examine Oborn (1960, p. 208) reported that the iron content of aquatic plant was much greater than that of land plants. The behavior of mangan ese is similar to that of iron in this respect, as indicated by publishe literature and work in progress (E. T. Oborn, written communicatio 1963). Cannon (1960) reported an average (obtained from publishe data on a wide variety of plant types) of 0.674 percent iron and 0.4815 percent manganese in the ash of plant parts.

Oborn (1960, p. 204) and other investigators point out that the amount of iron and other metals present in certain plant parts is greater than in other parts. The roots of some varieties may contain relatively large amounts. However, there also is a tendency for some accumulation in the leaves. Besides the differences from one part of the plant to another, there are seasonal changes in metal content of the leaves and other plant parts. Some species of plants are particularly effective accumulators of certain elements and contain much larger amounts than would seem to be required for metabolic purposes. Cannon (1960) and Lovering (1959) have reviewed literature relating to some of these plants. Bloss and Steiner (1960) found a positive correlation between the concentration of manganese in soil and underlying rock and the manganese content of leaves of the chestnut oak in Tennessee. They reported that the average manganese content of the ashes of leaves of trees in mineralized areas was 3.8 percent, and in nonmineralized areas was 2.1 percent. These values are considerably above the averages quoted by Cannon (1960) and suggest that the chestnut oak is a rather effective manganese accumulator.

Ljunggren (1951) found that spruce needles in the Vermland district of Sweden gave from 1.3 to 7.6 percent manganese in ash. The highest contents of manganese were found in the needles of trees growing in abandoned river channels, where manganese had been deposited and was available to the tree roots in large amounts.

Evidently a large amount of manganese can be removed from soils by forest vegetation; the amount returned annually to the soil by leaf shedding is also important. Levanidov (1957) estimated that 5 kg of manganese was returned annually to each hectare of the soil in birch forests in the south Ural region of Russia. About half the manganese in the leaves was readily soluble in water. If the area had an annual runoff of 10 cm and all the readily soluble manganese was carried in this runoff the water would have an average concentration of 2.5 ppm (parts per million) of manganese. Actually, most of the manganese would probably be adsorbed and retained by the soil and recirculated to the trees. However, if major runoff events occur during the season of the year when the ground in forested drainage basins is covered with freshly fallen leaves, rather large tonnages of manganese may be carried off in flood waters.

MANGANESE IN RIVER WATER

Konovalov (1959) reported an annual mean manganese content of 0.56 ppm for the Rioni River (whose basin contains extensive manganese deposits), 0.13 ppm for the Kura, 0.06 ppm in the Dvina and

Dnestr, and 0.04 in the Ob. These were the highest values reported—for other rivers of the USSR the average amounts of manganese were less, ranging down to a few micrograms per liter. Data on manganese content of major rivers in other parts of the world are being obtained through a program of the International Union of Geodesy and Geophysics. Preliminary results (W. H. Durum, written communication, 1963) show that manganese is always present, although concentrations greater than a tenth of a part per million are unusual.

Detailed records of the chemical composition of the water of many rivers in the United States have been published by the U.S. Geological Survey. However, except for a few rivers affected by industrial wastes and mine drainage, these records contain no information on manganese concentration. The amounts present in water that is subject mainly to natural processes of manganese solution and deposition cannot be ascertained from these data.

In a few areas where the manganese content of stream water was high enough to be objectionable when the water was used for a public or industrial supply, some analyses have been made. For example, Wiebe (1930) found from 0.04 to 0.13 ppm of manganese in the water of the Mississippi River at Fairport, Iowa, in a series of 10 samples taken between May 24 and October 19. More extensive future studies of minor constituents of water will be helpful in understanding more fully the natural processes by which manganese is brought into solution in river water.

The important role of vegetation in making manganese more readily available for solution in water of lakes and rivers seems to be well established by published information. Whether the dissolved manganese in river water is present as an organic complex, or in some other form, seems to be open to question. Theoretically, in aerated water whose pH is near 7.0, the maximum redox potential (as measured with a bright platinum electrode) that is likely to be reached will permit from a few tenths to more than one part per million of divalent manganese to remain in solution as Mn^{+2} at equilibrium. Consequently, it is not really necessary to postulate organic complexing, or stabilization of colloidal suspensions of oxide by organic solutes, in order to explain the presence of manganese in concentrations that probably are usually found in river water. In this respect the behavior of manganese is different from that of iron, for which solubility in aerated river water is normally very low.

Complexes of divalent manganese and organic anions are generally somewhat less stable than corresponding ferrous complexes. However, although references to the possible importance of organic complexes or chelates in stabilizing manganese against oxidation and precipitation in natural water are common in published literature, few actual data on manganese complexes with natural organic materials have ever been obtained. Serdobol'skii and Sinyagina (1953) noted that manganese complexes with citric, acetic, oxalic, and humic acids did not occur in soils whose pH was below 7.8, but that almost all manganese was complexed at pH 10.2. The writer has observed that, at a pH above 9.5, rather stable manganese oxide colloids are readily formed in laboratory solutions, and the apparent complexing action at high pH may be related to organic stabilization of colloidal oxides. In any event, a pH of 10.2 is higher than normally occurs in natural water, although it may be reached in some soils.

The literature contains a few implications that partly oxidized manganese species in natural water may be important. Ingols and Wilroy (1962), for example, mentioned the possibility of organic complexes in which the manganese was present as Mn^{+3} in river water. Almost no data on stability of trivalent manganese complexes have been published. Nightingale (1959) used a triethanolamine complex of trivalent manganese for spectrophotometric determination of the element, but the complex required a pH near 13 to be stable. In the present study, the manganese oxide precipitated at pH above 9.0 contained some manganese that was not oxidized to the +4 state. Possibly, colloidal oxide suspensions formed at very high pH consist of manganese oxide or hydroxide in which not all the manganese is at the +4 state. However, there is little reason to postulate forms of manganese other than the divalent state in explaining the presence of dissolved species. Until positive evidence of their existence is obtained, trivalent dissolved species need not be seriously considered.

STREAMBED MANGANESE OXIDE DEPOSITS

In certain areas of the world, deposits of manganese oxide, containing an admixture of iron oxide, form on rocks in the beds of streams. Such deposits occur, for example, in northern Maine (F. C. Canney, oral communication, 1962), in Summit County, Colorado (Theobald, Lakin and Hawkins, 1963), and in the Vermland district of Sweden (Ljunggren, 1953), and probably in other areas also. The processes by which manganese oxide is deposited in such areas are not fully understood. Possible mechanisms have been proposed by others, and further suggestions based on results of laboratory study will be presented later in this report. Deposition of manganese oxide from a dilute solution of manganous ions requires high pH and strongly oxidizing redox potential. The exact Eh and pH values required can be computed or predicted from graphic representations, such as those of the writer (Hem, 1963), if dissolved manganese activity is known.

The deposits in the Swedish streams have been rather closely investigated by Ljunggren (1953, 1955), and his data are more complete than any others known to the writer. Ljunggren's field studies were made during the summers of two successive years. On his first visit to the area, a considerable number of water samples were taken for determination of dissolved manganese, and pH measurements were made in the streams of interest. At that time, the streams were at a low stage of flow because there had been no rain for several weeks. On his second visit to the area, the streams were at a high stage of flow as a result of wet weather. No dissolved manganese data were obtained on this second visit, but pH measurements were made of the water in the streams.

Dissolved manganese concentrations at low flow were generally less than 0.10 ppm, although one stream contained about 0.3 ppm. The pH of streams where manganese oxide had been deposited generally ranged from 6.5 to 7.0. When the streams were at a high stage of flow, they had lower pH's, some less than 6.0. Direct precipitation of manganese at pH 6.0 from a solution containing 0.10 ppm of manganese would require a redox potential of 0.70 volts, which is higher than is normally attainable by the solution of oxygen from the air. Ljunggren reported that the oxide deposits seemed to be associated with a species of moss, *Marsupella aquatica*, which grew on the rocks. Whether the oxide was deposited as a result of influence on the system by the moss or because of microbiological growths associated with the moss was uncertain. The water was probably poorly buffered and the depletion of dissolved carbon dioxide in the vicinity of the vegetation during photosynthesis may have raised the pH of surrounding water to a level where the existing Eh would have been high enough to cause MnO_2 to be brought down even from the very dilute solution. The deposits reported in Maine and Colorado had no obvious algae or plant association, but the possibility of microbiologic influence cannot be ruled out.

Several questions regarding these streambed deposits of manganese oxide remain unanswered. If they occur as a result of photosynthesis, the deposition should show seasonal and posssibly diurnal cyclic effects, and perhaps a good deal of re-solution of the deposits during the nongrowing season. It is also possible that deposition occurs mostly during certain periods when the stream water contains more manganese or has a higher Eh or pH than usual. Analysis of a series of samples of the stream water collected at different seasons might help solve these questions.

All the streambed deposits of manganese oxide which have been analyzed contain considerable amounts of ferric iron, and apparently the iron oxide can be predominant. This fact, which would seem to have an important bearing on the mechanism by which the precipitates are formed, is considered later in this paper (p. B38).

Ljunggren (1955) reported that the streambed deposits contained many minor constituents, apparently because the negatively charged surface of the oxide tends to adsorb cations from the solution in contact with it. Among the more abundant minor constituents were barium and strontium. The oxide was somewhat radioactive, probably owing to the presence of radium. Probably these ions were retained at the oxide surface by adsorption. Cobalt, nickel, and vanadium were also present but, inasmuch as these ions are nearly the same size as the managanese and iron ions in the oxide lattices, they may be incorporated in the structure of the oxides rather than being removed from solution by adsorption.

The adsorption of barium by precipitates of manganese dioxide was briefly studied in the laboratory by the writer. The results suggest that the percentage of barium in solution that is adsorbed is a function of pH and that below pH 7.0 the adsorption is weak. The degree to which the oxides are enriched in barium may be an approximate index of the pH at the site of precipitation of the oxides. The fact that the deposits studied by Ljunggren contained a considerable amount of barium may be additional evidence supporting the idea that the moss associated with the deposits raised the pH of water adjacent to the plants and thus promoted the deposition of manganese.

MANGANESE IN LAKES AND RESERVOIRS

The highest concentrations of dissolved manganese in surface runoff are likely to occur in forested areas where the soil and underlying rocks are manganese bearing. In recently glaciated regions, drainage patterns are generally poorly formed and there are many lakes. Where there are lakes in regions favorable for manganese to be present in surface water, many interesting phenomena have been reported.

Because stable thermal stratification generally occurs in lakes during summer months, the supply of oxygen in the near-surface water derived from the atmosphere may not be circulated into the deeper water. In a lake supporting appreciable amounts of biological growths, the deeper water has an oxygen demand because organic debris is attacked by oxidizing organisms at and near the bottom. During the period of stratification the dissolved oxygen of the deeper water may thus be depleted and the environment made relatively reducing and favorable for increased solution of iron and manganese. Increases in iron and manganese content with depth in lakes during the summer stratification period are well documented. Hutchinson (1957, p. 809), for example, reports observations on Linsley Pond, Conn., showing manganese in excess of 3 ppm at moderate depth, and states that manganese concentrations can be expected to increase at conditions less reducing than are required for solution of iron. In this particular set of observations, the iron in solution exceeds the manganese content near the bottom of the lake.

Mixing of the lake water, which generally takes place seasonally, raises the redox potential of the deep water and can generally be expected to cause iron and probably manganese to precipitate. Because outflow from a lake is generally of the relatively oxidizing water at the surface, depleted in manganese by biochemical action, the lake can be considered a site for accumulation of the manganese brought in by the surface runoff. This managanese contribution includes dissolved Mn^{+2} species that would be detected in a chemical analysis of the water and also some contributions that might not normally be detected. For example, some manganese might enter the lake in suspension in the surface water, either adsorbed by sediments or contained in organic debris. There might also be an important amount of manganese brought in by ground-water inflow. Although the general long-term trend will favor manganese accumulation, the changing conditions within the body of water will sometimes favor high concentrations in solution and at other times low concentrations.

Where accumulation of manganese is rapid, a condition usually accompanied by rapid iron accumulation, the lake deposits may constitute a source of ore. Ljunggren (1953, 1955) described bog ores consisting of iron and manganese in the Lakes Tisjon and Grycken in Dalecarlia, Sweden. Some of the lake-bottom areas were particularly favorable for manganese deposition, and MnO_2 contents as high as 30 percent were reported for some of the deposited oxides. The deposits richest in manganese occurred in shallow water at depths between 1 and 2 meters, where the lake beds were permeable gravel, and it was suggested that ground water especially rich in manganese may have entered the lake in these areas. The Eh and pH of the lake water probably would have favored oxidation and precipitation of manganese from this inflow. Ljunggren believed micro-organisms were involved in the oxidation process, and the deposits contained considerable amounts of organic matter.

Deposits of manganese oxide on pebbles in lakes of Nova Scotia were mentioned by Kindle (1936) who attributed them to the action of algae. Krotov (1950) has discussed iron and manganese deposition in lakes in other parts of northern Europe. The topic is discussed in a general way by Krauskopf (1957) who has summarized processes which may lead to separation of iron and manganese in nature.

Small amounts of manganese in public water supplies are highly objectionable. The limit of 0.05 ppm for manganese given in the suggested U.S. Public Health Service Standards (1961) for drinking water may be too high for some industrial water. Griffin (1960) suggests that as much as 0.02 ppm manganese may be tolerated in the average domestic supply. Because the oxidation of manganese is a rather slow reaction under conditions generally reached in water treatment processes, the reaction may not be completed in the time the water can be held in the treatment facilities, and water containing small amounts of manganese can give rise to deposits of oxide in waterlines and other parts of the distribution system after the water has been filtered and chlorinated. The deposits of manganese oxide may be dislodged or partly redissolved at later times to give sudden increases in manganese content in water from the mains at some places.

Public water-supply reservoirs on streams, like natural lakes, can be expected to serve as accumulating basins for manganese. For reasons that have already been outlined, some of the accumulated manganese obviously could be released to solution at times; as this release occurs, occasionally water in the deeper parts of the reservoir or sometimes even the whole lake may contain objectionable concentrations of manganese. Intakes for water-supply systems are usually located at a considerable depth below the reservoir surface, to avoid wide temperature fluctuations, and for other reasons. This placement of intakes increases the probability of obtaining manganese-bearing water from time to time.

Although it seems evident that a few hundredths of a part per million, or more, of manganese might very often be found in water near the bottom of a reservoir, when the concentration of manganese of the inflow and of near-surface water in the reservoir is much smaller, this fact is not widely recognized.

Published literature indicates that the owners of water-supply reservoirs did not expect problems of excessive manganese in the water. When such problems did occur, various theories were suggested to explain the presence of manganese. Many of these speculations were erroneous. Because the inflow to the reservoir did not have a high manganese content at the time the water withdrawn did, it was assumed, for example, that the manganese originated within the reservoir. It was sometimes assumed the problem would disappear after a reservoir had been used for a time. Unfortunately, there is usually no sound reason to expect this to occur. On the contrary, the general tendency will be for manganese accumulations to increase with time.

Although sources of manganese probably differ from place to place where the problem is found, the general principles which govern the occurrence of manganese in water-supply reservoirs include:

1. Biological growths remove manganese from aerated water and precipitate it to the reservoir bottom.
2. Biochemical action in bottom mud and adjacent water may cause reducing conditions which periodically will return manganese to solution.
3. In regions where manganese oxides are present in considerable amounts as constituents of soil and of outcropping rock, the solution of manganese from submerged surfaces within the reservoir may be important. However, the reservoir will tend to accumulate any manganese brought to it in solution as the result of leaching of soil and organic debris. The rate of accumulation would be rapid in such an area.

DESERT VARNISH

Another form of manganese and iron-oxide deposits on rock surfaces which has received a good deal of attention over the years is the dark-colored coating called desert varnish which occurs on exposed rock surfaces and on surficial gravels in arid regions. There has been considerable debate as to the role of plants and other organic factors. The earlier investigators seemed generally to favor the view that the deposits are brought about largely, if not entirely, by primitive plants such as lichen. Some of the more recent investigators, however, have minimized the importance of the biochemical factor. Engel and Sharp (1958) in an extensive study of desert varnish in the Mohave Desert of California concluded that the deposits on the gravel of "desert pavement" came from underlying soil and were deposited from solution, and, that such coatings can be formed fairly rapidly (in one place within 25 years). Usually, however, the deposition process is much slower. Deposits on larger areas of bare rock were attributed to weathering solutions from rainfall, runoff, and dew, and to precipitation of airborne particulate matter. Although Engel and Sharp do not entirely dismiss the idea that lichen can play a part in the formation of desert varnish, they apparently do not believe that organic processes are a major factor. Deteriorated varnish coatings were noted by Engel and Sharp. In most instances, coatings that were being destroyed were flaked off as a result of weathering of underlying rock. Apparently the coating represents a residue resistant to weathering and probably is mechanically removed where water is more abundant.

Hunt (1961) has expressed the opinion that desert varnish deposits have not been actively forming in most of the Western United States during the past 2,000 years. This conclusion is based on archeological evidence for the most part, and it is suggested that desert varnish forms readily only when plentiful supplies of moisture are available.

The chemical environment for deposition of manganese and iron oxides on streambed rocks probably is much different from that prevailing in the occasional film of water on the surface of a rock on the land surface of a desert. However, the deposits have some points of resemblance in their minor-element content. These resemblances are probably related to the surface characteristics of ferric hydroxide and manganese dioxide. The anlyses of Engel and Sharp for minor constitutents of varnish are more complete than the data for the streambed deposits. Both, however, show strong enrichment of barium and somewhat similar amounts of cobalt, nickel, and vanadium. Desert varnish evidently contains more barium than the streambed deposits do. A rather high pH in the thin surface film of water on the rocks is certainly not unlikely.

DEEP-SEA NODULES

Manganese oxide is a principal constituent of nodules that occur at the bottom of the oceans in many places. These nodules and the factors causing them to be formed have been extensively studied. A recent report by Goldberg and Arrhenius (1958) suggests that the nodules form through accretion of oxidized manganese and iron on a suitable surface. The oxidation is attributed to effects of dissolved oxygen in the sea water. Redox potentials and pH in deep ocean water apparently are generally favorable for manganese precipitation. Willis and Ahrens (1962) have discussed the composition of the nodules. The effectiveness of manganese oxide in adsorbing metal cations is strongly indicated by these data.

SEPARATE PRECIPITATION OF IRON AND MANGANESE

Although the manganese oxide deposits considered here generally contain a considerable proportion of iron, the predominance of manganese in many can be explained only by some mechanism favoring the precipitation of manganese, rather than iron, from solutions containing both elements. It is difficult to postulate such a mechanism for the two elements' chemical behavior is somewhat the same. A solution of the two might be expected to yield a precipitate of both iron and manganese oxides when subjected to an increased Eh and (or) pH. Because iron is the more readily oxidized, however, the iron would tend to be removed first, and if a very high pH and redox potential are reached, the manganese will be oxidized and precipitated also. Krauskopf (1957) considered possible mechanisms for deposition of relatively pure manganese oxides and concluded that the precipitation of iron first and later precipitation of manganese from the same solution was a reasonable possibility. However, he pointed out that this theory implies that a considerable volume of deposited iron oxide should be somewhere near all or most manganese oxide deposits and that this condition does not always seem to exist.

The lakebed and streambed deposits of manganese oxide which have been considered here are actually all rather rich in iron, and some actually contain more iron than manganese. Processes of coprecipitation, perhaps with some degree of enrichment with manganese, seem adequate to explain them.

In surface streams the pH will normally be near neutrality, and Eh will seldom exceed 0.50 v except where unusual biochemical or other factors intervene. Stability field diagrams for the two elements (Hem, 1960a, 1963) show that manganese is soluble to the extent of more than 100 ppm at pH 7.0 and Eh 0.40 v, whereas iron under these conditions can be dissolved only to the extent of about 0.0001 ppm. This striking difference in solubility suggests that in weathering and related processes the two elements can be expected to show different behavior, that the change from an environment favoring iron deposition to one favoring manganese deposition may be a major one, and that a considerable separation in space may be involved. The presence of such an effective means for separating the elements readily explains the occurrence of some nearly pure deposits of manganese.

It is possible to precipitate manganese from a solution in which iron apparently is present in an amount comparable to or in excess of the amount of manganese present in solution. Under some conditions the apparent iron concentration may be mostly in an unreactive form. As pointed out elsewhere by the writer (Hem and Cropper, 1959), the iron reported in most analyses of river water must usually represent either a colloidal variety of ferric hydroxide or iron held in an organic complex. Because of the very low solubility of iron in waters having the usual pH and Eh of surface streams, the amount in ionic solution must be small. The colloidal particles of ferric hydroxide have a negative surficial charge at neutral pH, and the colloid is relatively stable and is not attracted to most mineral surfaces. Neither the colloidal hydroxide nor the organically complexed iron would be able to participate actively in chemical reactions, and could, therefore, be transported readily in the flowing water. Manganese, on the other hand, is likely to be in solution as Mn^{+2}, or possibly as the inorganic complex ions $MnHCO_3^{+1}$ or $MnSO_4^0$, because these forms are favored in the near-neutral oxidizing solutions of river water. Manganese oxide colloids are favored ly by a very high pH. Organic complexes of manganese are, in neral, less stable than corresponding ferrous complexes (Hem, 63).

In view of these factors, then, manganese should be present in river ater in a form susceptible to chemical reactions that can cause position as oxide even though the apparent content of iron in the ater is comparable to or greater than the manganese, and it is likely be present in a form readily available to aquatic life. The col- oidal iron would not be affected by such reactions, being already idized. The organic complexes of ferrous iron appear to slow the idation of the iron greatly (Shapiro, 1958; Hem, 1960b), and thus prevent it from being precipitated.

MANGANESE IN GROUND WATER

The chemical behavior of manganese in ground water can be pre- icted approximately by applying theoretical chemistry. The gen- ral principles and the relationships which are important here are vered in detail in an earlier paper (Hem, 1963).

In ground water systems the source of manganese for solution may from minerals in which manganese is a relatively minor constitu- t. In evaluating such systems, chemical equilibrium involving sim- manganese minerals, such as oxide, carbonate, or sulfide, cannot assumed. Equations and equilibrium diagrams may, therefore, t be directly applicable unless the ground water is precipitating, is in contact with, one of the simpler manganese minerals at or ar the point at which a water sample may be obtained.

Thermal springs which yield water containing from a few tenths several parts per million of manganese are fairly common. Some these waters are apparently associated with deposits of manga- e oxide. Others may possibly be associated with rhodochrosite $(MnCO_3)$ below the surface, for this mineral is sometimes found in in deposits. A few analyses were available in the U.S. Geological rvey files in Denver which represent samples where the pH was asured in the field at the time of collection. These analyses were amined for adherence to the equilibrium:

$$MnCO_3c + H^{+1} \rightleftharpoons Mn^{+2} + HCO_3^{-1},$$

here activity coefficient and complexing corrections were used on reported concentration data. Of a group of five analyses so amined, the total calculated manganese solubility checked fairly osely with the observed manganese concentration in only two. One these analyses represented the drainage flowing from an aban- ned mine near Silverton, Colo., and the other was for Pinkerton

Springs, a thermal spring in La Plata County, Colo. The other waters were all below saturation with respect to rhodochrosite by a wide margin.

No very specific conclusions can be drawn from these results. More information as to mineral species that may exist in the areas from which the water samples came would be needed before much use of the equilibrium equations with field data would be possible.

Much manganese-bearing ground water probably has been in contact with manganese oxide. Alluvium deposited by streams may contain sand and gravel incrusted with manganese oxide. Ground water circulating through this alluvium would dissolve some manganese. In areas where vegetation is plentiful and the surface drainage pattern includes many lakes, accumulations of manganese will form, probably as oxide, and at a later period these may become available to circulating ground water. This kind of condition seems to be common in the part of the United States which was subjected to glaciation in Pleistocene time.

Manganese commonly occurs in ground water in alluvium. Gidley (1952) described a number of collector-type wells along the Ohio River between Wheeling and Huntington, W. Va. Two wells at Parkersburg, W. Va., yielded water that contained 1.8 ppm of manganese. These wells obtained their water through horizontal pipes extending into gravel below the bed of the river. Although the manganese in the water from these wells evidently was not expected, manganese can be expected in the alluvium, especially in this area. The Ohio at Newell, W. Va., contained an average of 0.36 ppm manganese during the year ended September 30, 1957, and 0.03 ppm for the same period at Florence, Ind. The manganese entered as a result of acid mine drainage and other pollution along the Ohio and its tributaries upstream. The analytical data for stations on the river in this region were published by the U.S. Geological Survey (1960), and the results for 1957 as well as those for the 5 previous years show that manganese is being lost from solution and probably accumulates in the bottom sediment, especially in ponded sections.

The sediment along the Mississippi River in some places also yields water that is high in both manganese and iron. Well-known instances of the occurrence of manganese in wells adjacent to the river occur at Brainerd, Minn., and La Crosse, Wis.

LABORATORY STUDIES OF MANGANESE DEPOSITION

Experiments were designed to determine more closely some of the conditions which may control the deposition of manganese oxide on the surfaces of certain rock minerals.

NATURE OF SANDS UTILIZED

Experiments were performed with two different types of sand hich were available in the laboratory. One of these (sand 1) was purified silica sand obtained from the J. T. Baker Chemical Co. his material was almost pure SiO_2 and had uniformly well-rounded rticles. The range of particle diameters was from 0.8 to 0.25 mm or 95 percent of the material, and none of the particles had diameters ess than 0.1 mm. The cation-exchange capacity of the sand was too nall to be reliably measured.

The second type of sand hereafter called "sand 2" was a Monterey, lif., beach sand whose particles were moderately rounded and well orted, 85 percent having diameters between 0.8 and 0.25 mm. None ere larger than 0.8 mm and none smaller than 0.10 mm. The approximate composition of the sand was determined by means of staining technique and a grain count as:

	Percent
Quartz	45
Orthoclase feldspar	21
Plagioclase feldspar	34

he cation-exchange capacity of the sand was determined by equilibrating a weighed part with a 1.0 molar solution of $MnCl_2$. The sand as washed with ethyl alcohol to remove adhering manganese chloride; the adsorbed manganese was removed with 1.0 molar HNO_3, and etermined by the periodate procedure. The exchange capacity determined in this way was 0.66 meq (milliequavalent) per 100 g.

CATION-EXCHANGE ADSORPTION OF MANGANESE

The extent to which manganese behavior in natural water may e influenced by cation-exchange reactions has a considerable potential ignificance, and some experiments were made to determine the trength of adsorption of manganese on the sand surfaces as compared o the strength of adsorption of calcium.

A convenient-sized exchange column was prepared of sand 2 hrough which solutions could be passed under conditions of unsaturated flow. About 200 g of sand was placed in a glass tube 60 cm long nd 2 cm in diameter. The upper end of the tube was enlarged o a diameter of 4 cm over a length of about 10 cm. This enlarged rtion served as a reservoir for solution being passed through the olumn. The lower end was closed by means of a stopcock and the nd was retained in the tube by a fritted glass disc just above the topcock.

The volume of the 200 g of sand in the column when dry was 128 . A volume of 47 ml of water was required to saturate the 200 g of sand, and no change in volume of sand was observed. The void space in the column, therefore, was 47 ml or 37 percent of the sand volume, and the sand-water mixture was 23.5 percent water by weight.

The column was supported in a vertical position and solutions were passed through it by gravity. This arrangement permitted unsaturated or intermittently saturated flow. When solutions were passed through the column, a flow rate of about 200 ml per hour was generally attained after the water had flushed out most of the air from the sand column; a head of about 5 cm of water was maintained above the top of the sand surface. Slower rates were obtainable by partly closing the stopcock at the bottom of the column; however, the rate of water movement was not closely controlled.

Before it was put in the column, the sand was saturated with sodium by agitating it in a 1.0 molar solution of sodium chloride. Excess salt was removed by washing with distilled water, and the sand was dried on a steam bath before filling the column. This procedure was intended to remove any adsorbed divalent cations from the sand surfaces.

A solution of known calcium and manganese content was prepared from stock solutions of calcium chloride and manganous chloride and was poured into the column. All the effluent was collected in successive 100 ml parts, and the dissolved calcium and manganese contents in each part were determined. When the concentrations in the effluent became the same as those of the solution being put into the column, the flow was stopped and a new solution containing different amounts of calcium and manganese was made up. The new solution was used to repeat the experiment. Generally, between 2 and 3 liters of solution had to be passed through the column before equilibrium was reached. Solutions used had initial calcium concentrations near 100 ppm and near 10 ppm and Ca:Mn mole ratios ranging from 250 to 1.3. One solution containing 1.0 ppm Ca and 10 ppm Mn also was used. All the solutions had a pH of about 6.5. No loss of manganese by oxidation would be anticipated in these solutions and none was observed.

From the calcium and manganese content of the effluent, the amounts of these ions absorbed in the column were calculated, in milligrams and in milliequivalents. The results are given in table 1.

Amounts of calcium and manganese adsorbed are generally between 0.3 and 0.4 meq per 100 g of sand, which is about what would be expected, considering the rather dilute nature of these solutions. When the two ions are present in near-equivalent amounts (solution 5) the ratio of adsorbed calcium to adsorbed manganese is somewhat less than the mole ratio of dissolved calcium to dissolved manganese. This relationship indicates that the sand adsorbs manganese somewhat more strongly than calcium.

TABLE 1.—*Equilibrium concentrations of calcium and manganese in solution and adsorbed on feldspathic sand*

Solution	Mn (ppm)	C_{Mn} (mol per 1)	Ca (ppm)	C_{Ca} (mol per 1)	$C_{Ca}:C_{Mn}$	X_{Mn} (mg)	X_{Mn} (meq)	X_{Ca} (mg)	X_{Ca} (meq)	$X_{Ca}:X_{Mn}$	p	k
------	0.50	9.1×10^{-6}	92	2.3×10^{-3}	250	0.95	0.035	13.7	0.685	20	1.85	1.1
------	1	1.8×10^{-5}	92	2.3×10^{-3}	130	1.55	.056	13.6	.680	12		
------	10	1.8×10^{-4}	93	2.3×10^{-3}	13	4.67	.170	12.8	.640	3.8		
------	10	1.8×10^{-4}	1.0	2.5×10^{-5}	.14	12.60	.459	3.3	.165	.36	------	----
------	10	1.8×10^{-4}	9.2	2.3×10^{-4}	1.30	8.80	.320	7.1	.355	1.1	2.48	1.1
------	1	1.8×10^{-5}	9.2	2.3×10^{-4}	13	4.66	.170	9.4	.470	2.8		
------	.65	1.2×10^{-5}	9.2	2.3×10^{-4}	19	4.10	.149	9.3	.465	3.1		

The equilibrium reached in the exchange-column experiment can be written

$$CaX + Mn^{+2} = Ca^{+2} + MnX$$

where X represents the cation-exchange complex. The mass-law equilibrium expression:

$$K = \frac{[Ca^{+2}]\,[MnX]}{[CaX]\,[Mn^{+2}]}$$

cannot be strictly applied to the results, however. Apparent equilibrium constants for the seven sets of data in table 1, based on molar concentrations in solution and moles of ions adsorbed, range from 0.39 to 12.9.

The results of the experiments, however, do fit the empirical equation of Rothmund and Kornfeld:

$$\frac{C_{Ca}}{C_{Mn}} = \left(\frac{X_{Ca}}{X_{Mn}}\right)^{p} k$$

where C terms are molar concentrations of dissolved ions and X terms are equivalent quantities of adsorbed ions. The p and k terms are empirical constants.

In figure 1 where the ratio $C_{Ca}:C_{Mn}$ is plotted as abscissa and the ratio $X_{Ca}:X_{Mn}$ is plotted as ordinate, the data yield two straight lines, one for the solutions containing 92 ppm Ca, and one for the solutions containing 9.2 ppm Ca. The slopes of these lines provide a basis for computing the values of the exponent p in the equation. The value of k is the same for both sets of data. Because only one solution containing 1.0 ppm Ca was studied, there is no line for this concentration.

Because the experimental data are consistent with the idea that manganese losses and gains are associated with ion exchange rather than oxidation, it would seem that very little manganese oxidation

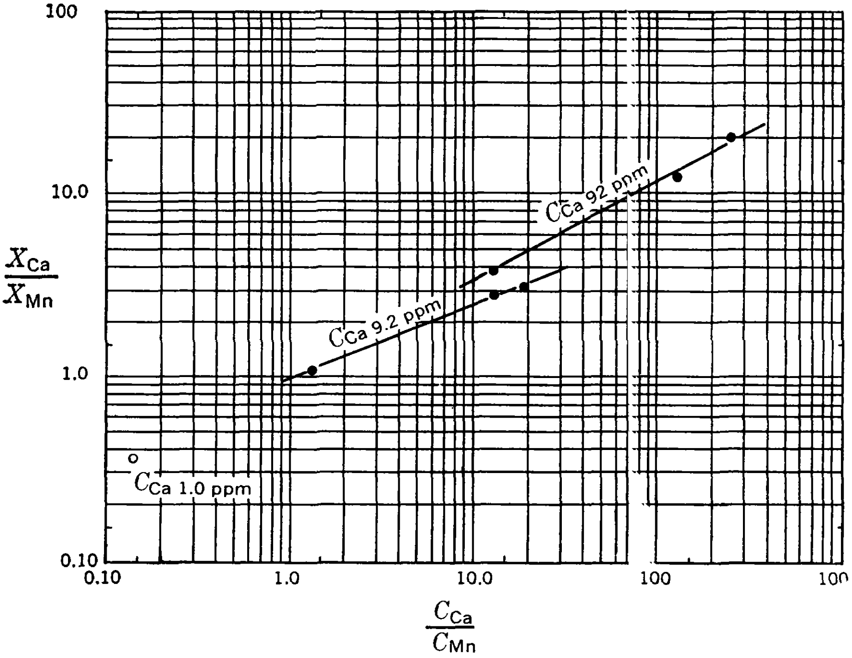

FIGURE 1.—Relationships among dissolved concentrations and adsorbed quantities of cal cium and manganese in adsorption column containing sand 2.

could have taken place. The experiments were run at a pH of 6.5, at which prior work showed the oxidation rate would have been very slow.

Figure 1 provides a basis for predicting certain features of the behavior of manganese in aquifers or in river or lake water in contact with sediment. Increases in calcium content of water in contact with sediment on which exchangeable manganese is present will tend to bring manganese into solution. The action of bacteria and the decay of organic matter in submerged soil often have the effect of bringing calcium into solution in immediate contact with the soil particles. This action could be a mechanism for increasing the manganese content of bottom water in reservoirs.

The results (fig. 1) further suggest that the ratio of dissolved manganese to calcium in ground water may be controlled by adsorption reactions in the aquifer material.

OXIDATION EQUILIBRIUM EXPERIMENTS

A volume of 3 liters of demineralized distilled water was brought to a manganese concentration of 10 ppm by adding manganese chloride. The pH was adjusted to 8.0 with sodium hydroxide. The solution was then transferred into six 500 ml-capacity polyethylene bottles. Five of these contained a measured quantity of sand 1, which had been thoroughly washed and dried beforehand. Amounts of sand present in the bottles ranged from 10 to 100 g. The remaining bottle contained no sand. The solutions were allowed to stand in the stoppered bottles.

From time to time, measurements of pH and Eh were made on each solution and a part was removed and filtered through a plastic membrane filter having 0.45 μ diameter pores. The amount of manganese remaining in solution in the filtrate was determined by the periodate procedure. The results of these observations are given in table 2.

TABLE 2.—*Manganese concentration, pH, and Eh of water in contact with silica sand*

Solution	Weight of sand (grams)	Time (hours)	Manganese concentration (ppm)	pH	Eh (volts)	
					Observed	Estimated
1	None	0	10	8.0	----	----
		17	9.6	7.2	0.36	0.43
		41	9.6	7.0	.39	.47
		137	10	7.0	.40	.47
		440	9.2	6.7	.50	.53
2	10	0	10	8.0	----	----
		17	9.4	7.2	.37	.43
		41	10	7.1	.40	.46
		137	10	7.0	.43	.47
		440	9.6	7.4	.46	.42
3	30	0	10	8.0	----	----
		17	9.7	7.5	.38	.38
		41	10	7.1	.41	.46
		137	10	7.0	.44	.47
		440	9.2	7.3	.49	.43
4	50	0	10	8.0	----	----
		17	9.5	7.1	.41	.45
		41	10	7.0	.42	.47
		137	9.2	6.8	.45	.51
		440	9.0	7.1	.48	.46
5	75	0	10	8.0	----	----
		17	9.2	7.0	.42	.47
		41	9.8	6.9	.42	.49
		137	8.8	6.7	.46	.53
		440	9.6	7.1	.47	.46
6	100	0	10	8.0	----	----
		17	9.3	6.8	.43	.50
		41	10	6.6	.44	.55
		137	9.4	6.4	.48	.57
		440	9.4	6.8	.50	.51

In an earlier experiment (Hem, 1963) with a similar set of solutions, except that no sand was present, oxidation took place at a pH of 8.0 or more, as evidenced by some loss of manganese, and equilibrium was attained after the solution had stood for a time. The chemical system represented by the data in table 2 can be visualized as involving divalent and oxidized manganese, dissolved oxygen and hydrogen ions, which will be related to each other at equilibrium by the Nernst equation. Because the solutions are dilute and interfering ions are absent, conditions may be evaluated with a stability-field diagram such as that developed in the writer's previous research in manganese chemistry (Hem, 1963). The value of Eh obtained from the graph for the observed dissolved manganese and pH is entered in table 2 as "estimated Eh."

When equilibrium is reached in the solutions, the calculated and observed Eh values should be in close agreement. Earlier work has shown that the experimental error in measuring Eh can be rather large, and this method of deciding whether or not equilibrium is attained leaves something to be desired. It is, nevertheless, a useful technique for studying oxidation reactions.

Although initial Eh was not measured, from the Eh-pH diagram it is evident that the initial solution was unstable and would tend to lose manganese by oxidation. Only a small amount of oxidation, however, is enough to lower the pH of the unbuffered solution substantially. When the pH goes down, the oxidation reaction almost stops but a considerable time is required to arrive at a state of equilibrium at the final pH.

The results in table 2 indicate that the above course of events was followed. The total loss in manganese, which was small in all the solutions, occurred in the initial 17 hours, while the solutions were standing overnight. The decrease in pH also occurred almost wholly in this period. The Eh measured in most samples at 17 hours, however, was below the equilibrium value. The slow return to equilibrium which followed entailed mostly increases in the redox potential and some minor fluctuation of pH.

Minor differences in behavior, possibly owing to presence of sand, could be discerned. Amounts of manganese lost were about the same in all solutions, but the solutions with more sand had higher Eh's. There was no definite indication in any of these data that the sand had an important effect on the rate or amount of oxidation occurring, and no further experiments were made with the quartz sand.

The next series of experiments was made using sand 2. The sand was prepared for use by stirring it in a 1.0 molar sodium chloride solution for several hours, the mixture was allowed to stand overnight, and the excess salt was washed from the sand with demineralized distilled water until the washings were chloride-free. This procedure was intended to fill exchange positions on the sand surface with sodium. Presumably, these positions would later be occupied by manganese.

Data given in table 3 were obtained in the first experiment with sand 2. The initial conditions imposed on the solutions reported on in table 3 were different in two respects from those affecting the data in table 2: (1) The initial pH in the solutions was 7.7 instead of 8.0; at this lower pH the rate of manganese oxidation would be lower. (2) Sand 2 had some adsorption capacity for cations which might be expected to remove manganese from solution.

TABLE 3.—*Manganese concentration, pH, and Eh of unbuffered solutions in contact with feldspathic sand*

Solution	Weight of sand (grams)	Time (hours)	Manganese concentration (ppm)	pH	Eh (volts)	
					Observed	Estimated
7	None	0	10	7.70	0.47	----------
		18	9.8	7.77	.41	0.34
		42	10	7.60	.47	.36
		114	10	7.25	.44	.43
		210	9.7	7.09	.45	.46
		354	9.9	7.07	.49	.46
8	10	0	10	7.70	.47	----------
		18	9.2	7.59	.43	.37
		42	9.0	7.11	.49	.46
		114	8.4	7.23	.45	.44
		210	7.4	7.24	.46	.44
		354	7.9	7.28	.47	.45
9	30	0	10	7.70	.47	----------
		18	8.3	7.41	.44	.40
		42	7.6	7.13	.50	.45
		114	6.4	6.77	.47	.52
		210	6.3	6.74	.48	.53
		354	5.9	6.95	.48	.49
10	50	0	10	7.70	.47	----------
		18	7.5	7.34	.45	.42
		42	5.7	7.05	.50	.48
		114	4.9	6.87	.47	.51
		210	3.9	6.95	.47	.51
		354	3.8	6.92	.49	.51
11	75	0	10	7.70	.47	----------
		18	7.0	7.43	.44	.40
		42	5.2	7.20	.49	.45
		114	4.3	7.00	.46	.50
		210	3.5	7.13	.46	.48
		354	3.8	7.22	.47	.46
12	100	0	10	7.70	.47	----------
		18	6.2	7.27	.46	.44
		42	3.8	7.01	.50	.50
		114	2.8	6.92	.46	.52
		210	2.4	6.96	.47	.52
		354	1.4	6.98	.48	.52

The results obtained with sand 2 show that the solutions in contact with this sand decreased considerably in dissolved manganese over the 354 hours of the experiment. The rate of loss of manganese was rapid for the first few days and became slower thereafter. Figure 2 shows the rate of loss of manganese in four of the solutions. Except for the solution having 100 g of sand, the dissolved manganese in the solutions did not change significantly after about 200 hours.

The loss of dissolved manganese from these solutions can be attributed either to adsorption by the cation-exchange surfaces of the sand or to oxidation of manganese, or to both. Any appreciable oxidation effect would be an indication of catalytic action by the sand surface, for no manganese loss occurred at this pH in the absence of sand. Because the pH changes in the unbuffered solution are small, it seems probable that there was only a small amount of oxidation, and that most of the effects observed in these solutions were the result of ion exchange.

EFFECTS OF SAND ON OXIDATION RATE

In order to obtain more information as to the relative importance of adsorption and oxidation in the loss of manganese from solutions in contact with sand 2, several additional test runs were made. The first set of solutions was made up as before, and sodium bicarbonate was added to give a concentration of 120 ppm bicarbonate. The bicarbonate was added in order to stabilize the pH in these solutions and to prevent it from decreasing as a result of oxidation and hydrolysis of manganese. The results of this series of tests are in table 4.

TABLE 4.—*Manganese concentrations, pH, and Eh of solutions containing bicarbonate ions in contact with feldspathic sand*

Solution	Weight of sand (grams)	Time (hours)	Manganese concentration (ppm)	pH	Eh (volts, observed)
13	None	0	10	8.03	0.40
		7	10	8.07	.40
		24	10	8.12	.38
		48	9.7	8.29	.39
		97	10	8.43	.40
		216	9.5	8.60	.37
14	10	0	10	8.03	.40
		7	8.6	7.95	.41
		24	8.7	8.07	.39
		48	8.1	8.18	.40
		97	8.1	8.38	.40
		216	6.9	8.39	.39
15	30	0	10	8.03	.40
		7	7.9	7.88	.42
		24	7.4	7.92	.40
		48	6.5	7.89	.43
		97	5.1	8.18	.41
		216	3.2	8.17	.41
16	50	0	10	8.03	.40
		7	7.4	7.82	.42
		24	6.0	7.78	.40
		48	4.9	7.75	.43
		97	3.6	8.07	.42
		216	2.1	7.90	.43
17	75	0	10	8.03	.40
		7	6.1	7.75	.43
		24	4.4	7.84	.40
		48	2.5	8.04	.41
		97	2.3	8.06	.41
		216	0.60	8.09	.41
18	100	0	10	8.03	.40
		7	5.7	7.71	.43
		24	3.8	7.70	.41
		48	2.2	7.93	.42
		97	1.2	8.10	.41
		216	.25	8.02	.41

The pH of the solutions in this experiment fluctuated about 0.3 pH unit (except for the solution containing no sand). This compares with a fluctuation of nearly a full pH unit in other tests. The rate of manganese loss was also more rapid than in the earlier experiment at a lower pH. The rate also was steady during most of the experiment. In figure 3, the relation time to manganese concentration is shown graphically. The rate of manganese loss is also apparently a function of the amount of sand present.

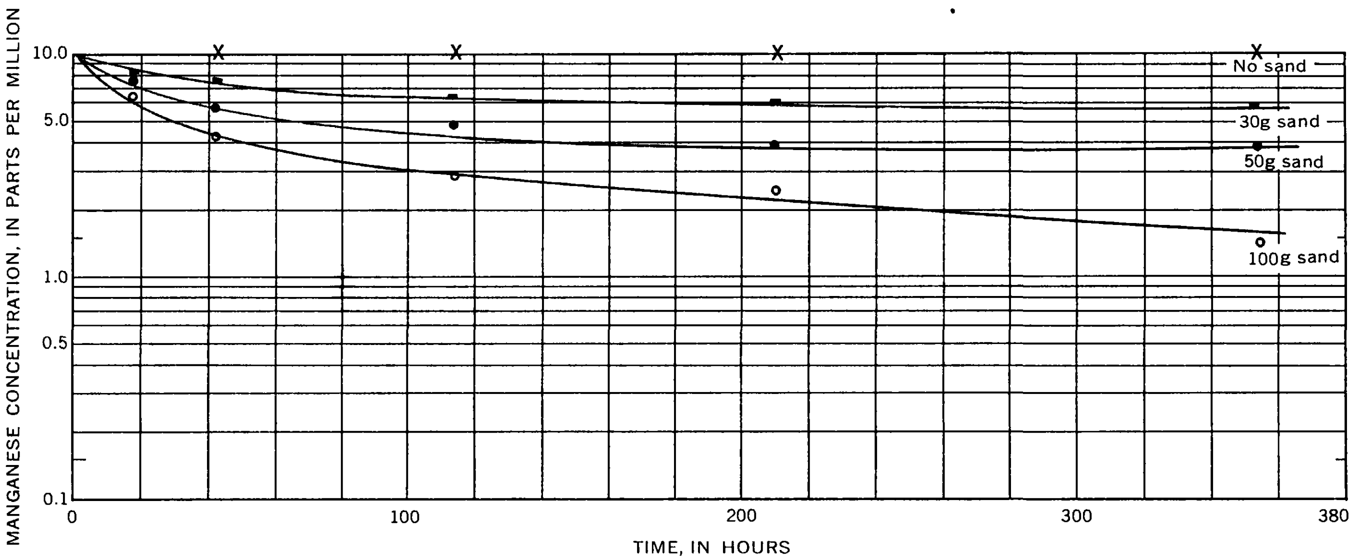

FIGURE 2.—Rate of loss of manganese from solutions in contact with sand 2. No bicarbonate added.

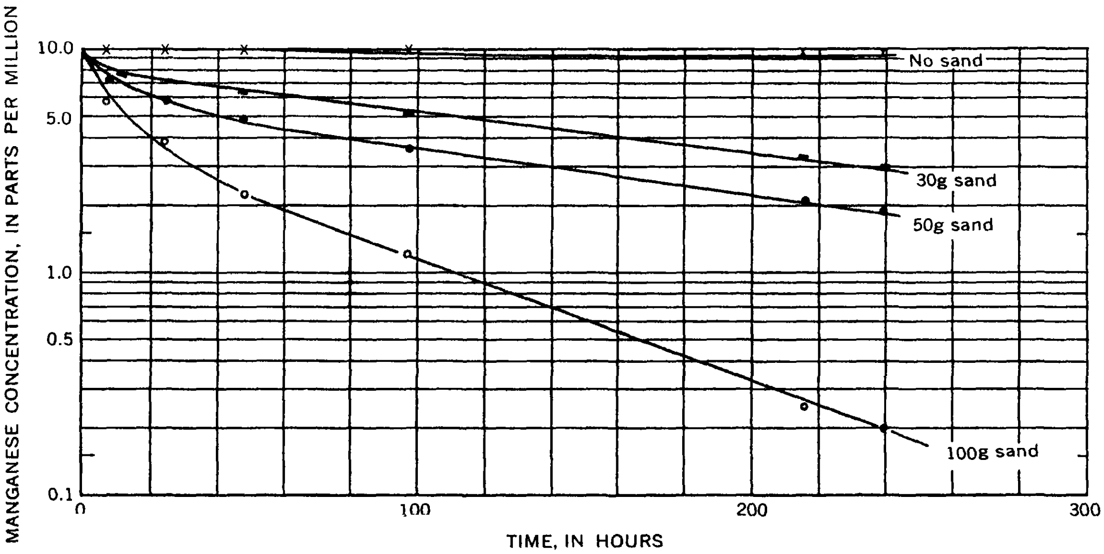

FIGURE 3.—Rate of loss of manganese from solutions in contact with sand 2. Bicarbonate concentration 120 ppm, initial pH 8.03.

The redox potential at equilibrium in the solutions containing bicarbonate was not calculated. With one exception, the manganese activity in each solution and the observed pH intersect in an area where manganese activity is controlled by the solubility of $MnCO_3$. This solubility is not a function of Eh. However, later experiments showed that manganese carbonate was not precipitated from these solutions to any significant extent.

The difference between the results shown in figure 3 and those from the previous experiment given in figure 2 suggests that oxidation of the manganese was a more important factor in solutions 13–18 than in 7–12. The difference in pH between the two experiments is enough to indicate considerably more oxidation in solutions 13–18 than in 7–12. However, it seems unlikely that the exchange capacity of the sand is very strongly influenced by pH in this range.

The results are most readily explainable as a combination of effects of cation exchange and oxidation. In both sets of solutions the decrease in dissolved manganese early in the experiment was rapid and is attributable to adsorption, perhaps with a small amount of concurrent oxidation. The rate at which manganese content of solutions represented in figure 2 decreased approached zero as the exchange reaction neared equilibrium. The solution containing 100 g of sand, however, showed a slow and steady loss of dissolved manganese, as represented by the straight part of the lowest curve in figure 2. This loss is attributable to oxidation, and appears to be a function of the sand surface available. Very little manganese was lost from the solutions containing less than 100 g of sand after the ion-exchange reaction had reached equilibrium.

The rate of manganese oxidation is known to be slowed in the presence of bicarbonate (Hem, 1963), and even though the pH of solution 13, which contained no sand, rose to 8.6, very little oxidation had occurred after 216 hours.

The rates of manganese loss shown in figure 3 are more rapid than those in figure 2, but the amount of manganese which remained in solution when the curves merged into straight lines was about the same in all the solutions that contained the same amount of sand. This general agreement supports the hypothesis that the initial loss of manganese is the result of ion exchange and the steady, slower rate attained later in the experiment was the result of oxidation, catalyzed by the sand surface and its relatively immobile layer of adsorbed manganese ions.

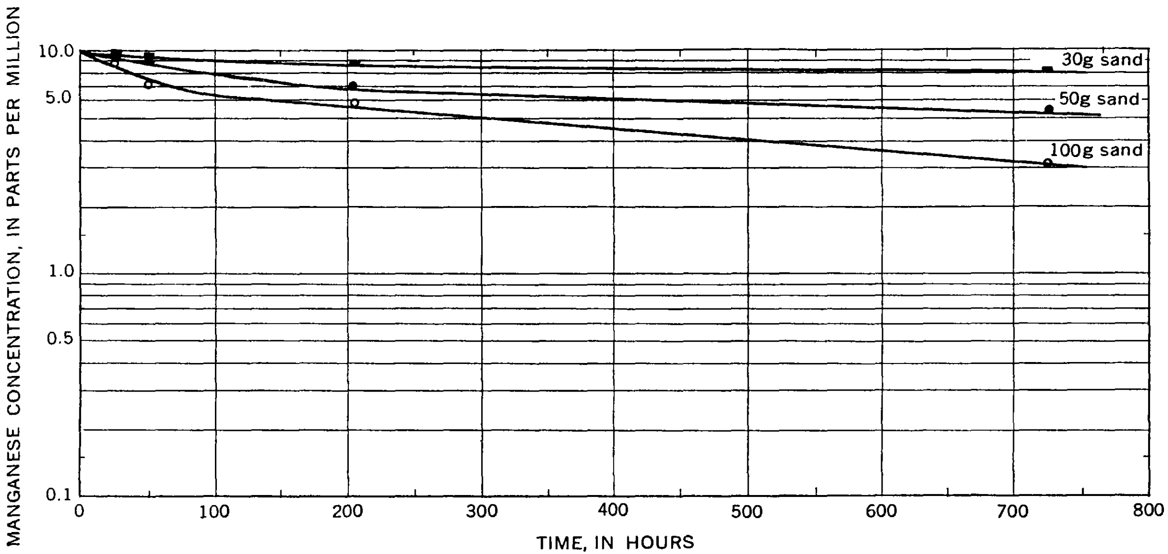

FIGURE 4.—Rate of loss of manganese from solutions in contact with sand 2. Bicarbonate concentration 120 ppm, sulfate concentration 2,000 ppm; initial pH 7.95.

Nine additional sets of solutions were prepared, by similar procedures, to evaluate the effect on manganese loss of such factors as pH and different amounts of sulfate and bicarbonate. The results obtained in a solution containing 2,000 ppm of sulfate, added as sodium sulfate, are given in figure 4. Large amounts of sulfate were found previously (Hem, 1963) to retard the oxidation rate, and the sodium would tend to compete with manganese for ion-exchange positions on the sand. The results in figure 4 are, therefore, to be expected—manganese loss was very slow in that particular experiment.

From one of the other sets of solutions it was learned that a bicarbonate concentration of 1,000 ppm brought about manganese removal from all solutions at the same rate, whether sand was present or not. These results indicate precipitation of manganese carbonate; the solubility product was considerably exceeded in these solutions. Other sets of solutions that gave faster manganese loss rates than the results in figure 3 had sulfate concentrations of 100 ppm and bicarbonate concentrations of 20 ppm.

The cation-exchange capacity of sand 2, measured by means of 1.0 molar manganese chloride, was 0.66 meq per 100 g. This value is not directly applicable to the much more dilute solutions used in these experiments. The amount of manganese in solution in each of the bottles was 5.0 mg at the start of the experimental runs. Manipulations during the study required the removal of most of the solution from the bottle to make Eh, pH, and manganese determinations, and only an approximate figure can be calculated for the amount of dissolved manganese removed from the system in this way. Hence, the total amount of manganese retained in the sand could not be accurately calculated. The results are of value as indicators of reaction mechanisms and oxidation rates as affected by the sand surfaces, but are not susceptible of strict quantitative interpretation.

To obtain a strict control of pH in the further study of oxidation rate, the problem was approached in a different manner. A solution containing 5.0 mg Mn^{+2} and 50 mg SO_4^{-2} in a volume of 500 ml was prepared from stock solutions of manganous chloride and sodium sulfate and boiled distilled water. It was adjusted to pH 8.50 by rapid addition of standard potassium hydroxide, and was maintained at this pH by addition of the base as required. The solution was stirred with a mechanical stirring device, and from time to time portions were removed with a pipet, filtered through a plastic membrane filter, and analyzed for manganese. The amounts of base added and elapsed time were recorded. The experiment was repeated at pH 8.82 and at pH 9.28. The sulfate was present to decrease the oxidation rate to a level at which it would be easy to study.

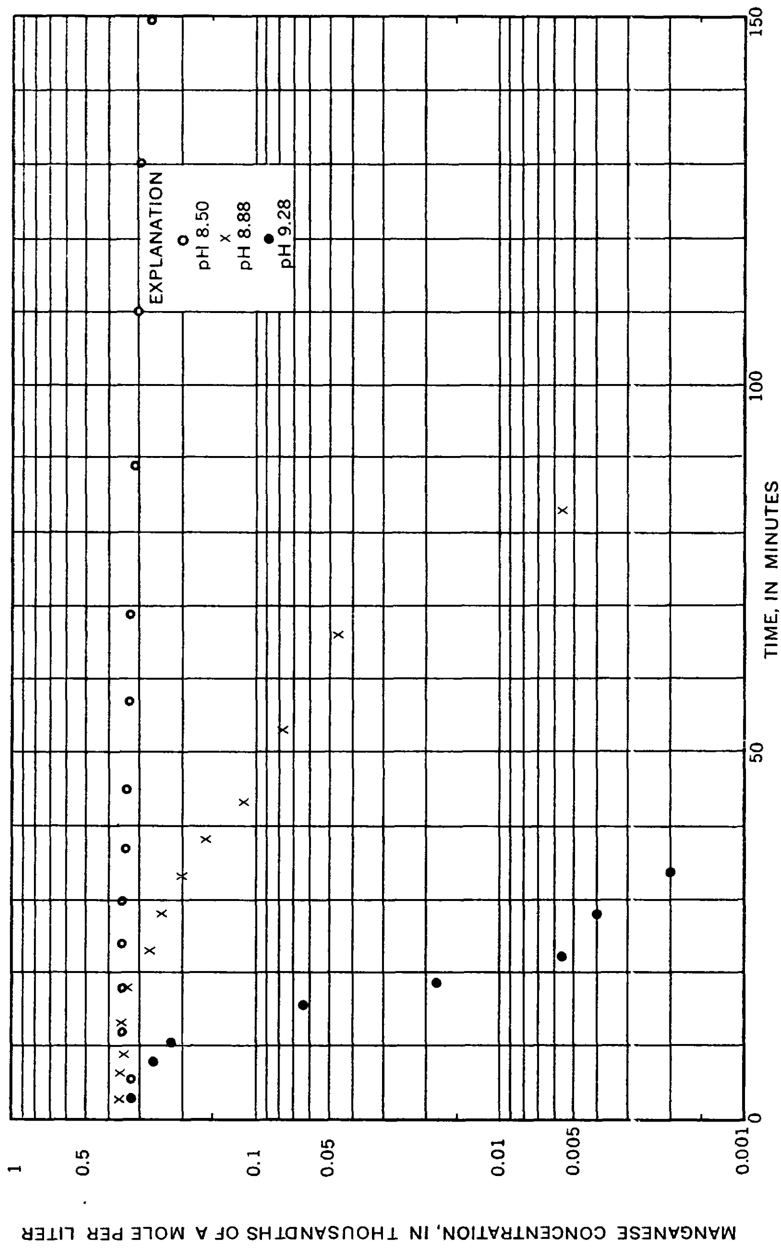

FIGURE 5.—Rate of loss of manganese from solution at three different pH levels. No sand, no bicarbonate, 200 ppm sulfate.

The results of the experiments are shown graphically in figure 5. When the pH was held at 8.50, the loss of manganese was slow but appeared to take place at a constant rate throughout the test. The half-time for the oxidation at this pH, calculated on the basis of an extrapolation of the results given in figure 5, is 306 minutes, equivalent to a first-order rate constant of 2.3 × 10^{-3} min $^{-1}$. At pH 8.88 and 9.28, the oxidation rates were not constant. In each of these two runs, after a short period of slow loss of manganese, the rate increased and a much higher rate of loss was maintained until almost all the manganese had disappeared from solution. The last few observations made in each of these tests suggest a possible further change in rate, but these results were probably influenced to some extent by difficulty in measuring small manganese concentrations accurately. Consequently, their significance is questionable.

The increase in rate is attributed to the autocatalytic effect of precipitated manganese oxide and has been observed before in this work (Hem, 1963). If the rates observed during the first 10 minutes at pH 9.28 and during the first 20 minutes at pH 8.88 are extrapolated, they give reaction half-times of about 15 minutes and 120 minutes, respectively. The first-order reaction-rate constants are 4.6×10^{-2} and 5.8×10^{-3}, and may represent the uncatalyzed oxidation rates at these pH levels.

Although later rates observed at these two pH's were not completely consistent, both sets of data show a period of fairly constant reaction rate. The rate constants for these sets are 2.5×10^{-1} at pH 9.28 and 4.1×10^{-2} at pH 8.88. The amount of increase in the rate brought about by the autocatalytic effect of oxide surfaces is substantial.

Two additional experiments were made to explore the effect of sand 2 on the rates of loss of manganese. These experiments were made under conditions identical to those of the preceding ones, except that 25 g of sand 2, which had been previously saturated with Mn^{+2} by exposure to 1.0 $MnCl_2$ and washed free of chloride with distilled water, was added to each solution before adjusting the pH to the level at which it was held constant. The sand grains were kept in motion by the stirrer. The rates of manganese loss in these solutions at pH 8.80 and 9.00 are shown in figure 6.

The autocatalytic effect which was so pronounced in the solutions that contained no sand is missing from the results shown in figure 6. The reaction half-time at pH 8.80 is 133 minutes and at pH 9.0 is 63 minutes, and a steady rate was maintained throughout the experiment in both solutions. When the difference in pH is considered, the rates were not significantly different from the initial ones observed in solutions that contained no sand. The reaction rate constants are 1.1×10^{-2} at pH 9.0 and 5.2×10^{-3} at pH 8.80.

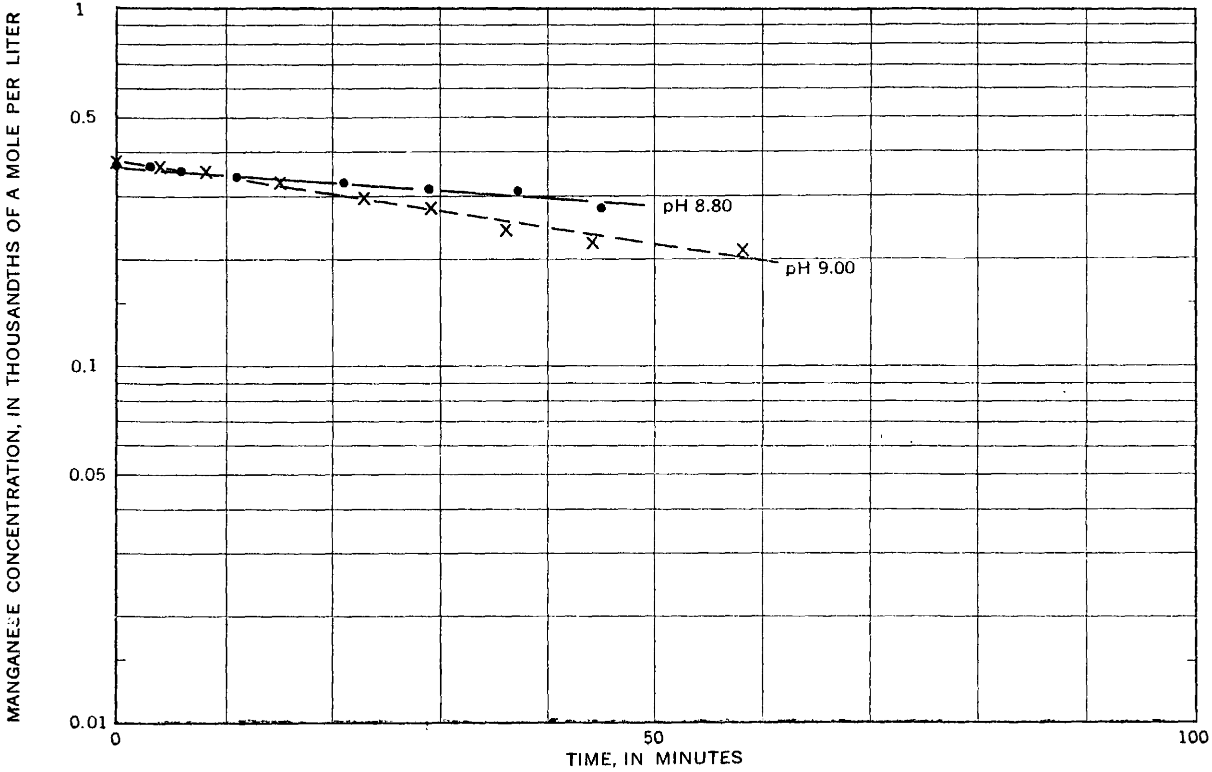

FIGURE 6.—Rate of loss of manganese from solutions stirred with 15 g of sand 2. Sulfate concentration 200 ppm, no bicarbonate.

Figure 7 is a graph showing first-order rate constants for the manganese oxidation reaction in aerated water, in relation to pH for solutions which contained no sulfate or bicarbonate (from laboratory studies made for Hem, 1963), and for solutions containing 200 ppm sulfate. The solid points represent the data for samples which contained sand. The effect of pH and sulfate have been noted previously.

The apparent inhibiting effect of the sand on the autocatalysis is of some interest. Several possible explanations may be suggested. The deposition of oxide on the sand surfaces evidently results in a material whose properties differ from the freely suspended particles of oxide that occur in solutions that contained no sand. Ultimately, perhaps a deposit would be built upon the sand grains that would be as effective in catalyzing the oxidation as the free suspended oxide, but the amount formed in this experiment was evidently not sufficient to do so. In addition to effects stemming from the physical nature of the oxide deposit, the oxidation at the sand surface may favor formation of an oxide chemically different from that formed in solution. As noted previously (Hem, 1963), the oxide formed between pH 8.5 and 9.5 is a mixed product, having a decreased proportion of tetravalent manganese at higher pH. It seems possible that the sand surfaces may alter what is a complex reaction mechanism and may promote the formation of the tetravalent oxide rather than the less highly oxidized species.

Possibly a larger amount of sand in the reacting solution would have changed the results. Because of mechanical difficulties in maintaining continuous motion of the sand, amounts much greater than those used in the experiment could not be utilized. The adsorbed manganese on the sand added another factor. Some of this manganese may have been replaced by sodium from the solution, but the ratio of manganese to sodium in the solution should have been high enough to prevent any important amount of replacement. Obviously, sand having a capacity of adsorbing more manganese would have obscured the results.

The results of this set of rate studies suggest that the sand affected the course of the oxidation reaction by inhibiting the autocatalyzed process which occurred in the absence of the sand. A further indication of this effect can be obtained from comparisons of relationships of OH^{-1} demand to manganese oxidation.

The amount of base consumed and corresponding amounts of manganese precipitated were calculated from the titration data. To obtain the amount of manganese lost by precipitation, the total amount present at each time of sampling for manganese content was calculated. This calculation required correcting for manganese removed in the sampling process. A satisfactory stoichiometric relationship was not obtained, however, perhaps partly because carbon dioxide was adsorbed

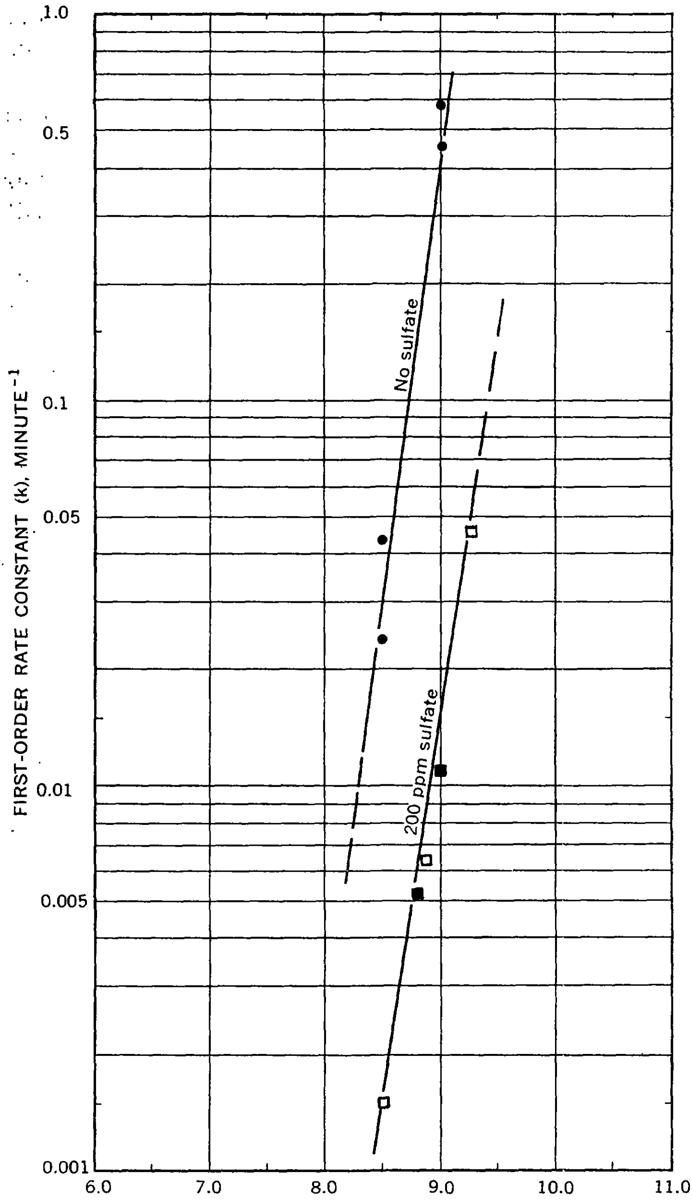

FIGURE 7.—Effects of pH and dissolved sulfate on rate of oxidation of manganese.

by the alkaline solutions from the air. Nevertheless, the results did suggest that considerably less of the standard base was required per unit of manganese oxidized at pH 9.28 than at pH 8.5. The amount of base consumed in the oxidation experiments where sand was present was greater than would have been expected at the same pH in the absence of the sand-grain surfaces. This fact is a further suggestion that the sand surfaces may promote the formation of MnO_2.

Although the magnitude of the catalytic effect of 15 g of sand 2 in 500 ml of solution appears to be small, the effect observed in the earlier experiments where 100 g of sand was present is evidently appreciable. The effect in the presence of the larger amount of sand and of bicarbonate ions can only be evaluated approximately. The rates obtained in earlier work (Hem, 1963) at pH 9.0, 9.1, and 9.3 are about the same, or slightly slower, than those in figure 6 representing solutions containing 200 ppm of sulfate. If these rates are extrapolated to pH 8.0, a value for k of about 1×10^{-4} min^{-1} is obtained. In the presence of 100 g of sand at this pH, the rate constant estimated from figure 2 is 1.9×10^{-4}. However, the actual oxidation rate at pH 8.0 in the presence of bicarbonate is not readily determinable, and the extrapolated value is probably not reliable.

ADSORPTION COLUMN EXPERIMENTS

The sands used in these experiments have a mean particle diameter of about 0.5 mm. The surface area per gram is therefore about 47 sq cm. The area of 100 g of sand is 4,700 sq cm. In a bottle containing 500 ml of water, this gives an area of sand of about 9.4 sq cm per milliliter. When the sand was just saturated with water the weight composition was 23.5 percent water and 76.5 percent sand. Hence, in an aquifer that was composed of this type of sand the surface area per milliliter of water would be about 140 sq cm. This area is about 15 times that available per milliliter of water in the bottles containing 100 g of sand.

In many aquifers a considerable amount of fine-grained material is present. Because the surface area of a sphere is proportional to the square of the diameter, an increase in proportion of small particles increases the area per unit weight very markedly. At the same time, the small particles decrease the space available for water in a unit volume of aquifer material. Consequently, the surface area of solids per milliliter of water in many aquifers is far greater than 140 sq cm, a value which is probably near the minimum for granular aquifers.

In order to duplicate more closely the solid-liquid relationships that occur in partly saturated or intermittently saturated sediments, some further experiments were performed with the adsorption column used earlier to determine the cation-exchange behavior of sand 2 toward manganese and calcium. A considerable volume of manganese solution was passed through the column and the cation-exchange positions on the grains were filled with manganese ions. The column was then drained and was allowed to stand undisturbed in the laboratory for several months. During this period, the upper part of the sand had become completely dry. Work with the column was resumed without disturbing the sand. In these resumed experiments, solutions of manganese chloride were used which contained about 100 ppm HCO_3^{-1} (added as sodium bicarbonate) to stabilize the pH. No calcium was present in the solutions. In general, the solutions were more alkaline than the ones used previously and had a pH ranging from 8.0 to 9.0.

It was immediately evident that manganese was being absorbed by the column to a greater extent than before, and even though large volumes of solution were passed rapidly through the column, the manganese content of the effluent did not reach the level of the original solution. Rather, the manganese concentration of the effluent seemed to reach a constant value considerably below the initial concentration. Furthermore, the total amount of manganese picked up by the column, about 75 mg, greatly exceeded the exchange capacity of the sand it contained. Evidently, manganese was now being rapidly oxidized in the column. As the experiments continued, the upper 10 cm or so of sand in the column became dark brown. This color was the result of deposition of a coating of oxidized manganese on the sand grains, and MnO_2 was shown to be present by X-ray diffraction analyses of the material.

The approximate rates of oxidation of manganese as solutions passed through the sand ranged from a half-time of about 10 minutes at pH 8.6 to about 120 minutes at pH 8.0. These values are inexact because the actual contact time of solution with the column is uncertain. Probably most of the oxidation occurred in the upper part of the column. However, these rates are appreciably faster than the ones indicated for pure water in figure 7. They are much faster than the ones observed for solutions containing bicarbonate in the absence of sand (Hem, 1963). The catalytic effect of the oxide coating on these sand grains is, thus, definitely indicated.

When solutions having a pH greater than 9.0 were passed through the column, some of the manganese oxide was dislodged from the sand grains and the effluent contained a brown colloidal suspension of manganese oxide.

When solutions containing 1.0 ppm Mn, having a pH below 7.0, were passed through the column, the oxidation reaction appeared to be reversed and somewhat higher concentrations of manganese were present in the effluent than had been in the original solution. Measurements of pH, Eh, and manganese content for two initial solutions and of the effluent discharged after constant manganese concentration has been reached are given below. The calculated values for Eh were determined from graphs of pH, Eh, and manganese activity published earlier (Hem, 1963). The close check obtained between observed and calculated Eh suggests the solution in the column had reached a state of oxidation equilibrium after about 600 ml had passed through.

		Eh (volts)		
Solution	*pH*	*Measured*	*Calculated*	*Mn (ppm)*
Input	7.21	0.47	0.49	1.0
Effluent	7.78	.45	.45	.1
Input	6.35	.50	--------	1.0
Effluent	7.18	.49	.49	1.2

The amount of oxygen present in aerated water at a temperature of 25° C is more than sufficient to oxidize 10 ppm of manganese. However, if larger concentrations of manganese are present, the availability of oxygen may become the principal factor affecting oxidation rate.

The control of pH in the column experiments was not very exact and the time the solution spent in the part of the column where oxidation was most active is uncertain. However, the average time required for half the manganese to be oxidized at pH 8.5 in the column appeared to be about 12 minutes. In an earlier experiment at pH 8.5 in aerated distilled water, the half-time for manganese oxidation was about 30 minutes. In the presence of 100 ppm bicarbonate activity the rate was much slower than this. The results of the column experiments are not sufficiently refined to show the exact magnitude of the catalysis effect in speeding the oxidation of manganese, but they do indicate that the effect is much stronger than where the area of sand per unit volume of solution is small.

An indication as to the reversibility of the oxidation process can be obtained from the column results. Establishment of equilibrium by introducing solution at pH 7.21, which involved oxidation and precipitation, required about the same time as the reverse equilibrium obtained by introducing a solution whose pH was 6.35. In the attainment of this equilibrium, manganese was reduced and dissolved.

APPLICATION OF LABORATORY AND THEORETICAL DATA TO NATURAL CONDITIONS

The laboratory work described in this paper gives some general indications as to the mechanisms that may be involved in the deposition of manganese oxides in natural environments and in the reduction and solution of such deposits in surface and ground water. A brief recapitulation of the possibilities is in order.

Because the work was concerned with inorganic chemical processes, the effects of aquatic plant or animal life were not considered extensively, though it is not to imply that the behavior of manganese as observed in nature is not extensively influenced by these life processes. The fundamental energy relationships that may be used to evaluate the chemistry of manganese are applicable to all environments.

The mineral fragments that constitute stream sediments, soils, and the sedimentary rocks have some cation-exchange capacity. In normal fresh-water environments the exchange positions are generally occupied by the common divalent cations of natural water. Manganese is likely to be present in this adsorbed material in somewhat greater proportion than in the solution at equilibrium. Adsorption-desorption equilibria may have considerable influence on the amount of manganese in solution in water in contact with sediments.

Deposition of manganese oxide coatings on mineral grains can be initiated when a bed of sand or a subsoil stratum through which manganese-bearing water has been moving becomes dry and remains so for a time. Renewed movement of manganese-bearing aerated water through this material can bring about localized deposits of manganese oxide in the areas where Eh is high enough. The oxidation process will deplete the dissolved oxygen of the water, and probably deposition of oxide will not occur very deeply in the zone of saturation, and in some instances would be possible only in the soil or subsoil zones where water moves generally by unsaturated flow.

The behavior of divalent manganese that may be brought into contact with manganese oxide will be controlled by three fundamental variables, pH, Eh, and dissolved manganese activity. Increases in any one of these variables above the level at which the initial deposit of oxide was formed will bring about further deposition of oxide, and decreases in any one of the three variables will cause the deposited oxide to go back into solution. These general principles should help explain the occurrence of manganese oxide deposits in lakes, streams, and elsewhere, and the occurrence of water in reservoirs, both surface and underground, which contains excessive quantities of manganese. Although literature relating to these occurrences is abundant, it is generally difficult to determine from published descriptions which factors are principally responsible for high manganese concentrations and the formation of oxide deposits, because field observations and measurements are almost always inadequate. Measurement of Eh in the field is generally difficult and in some environments is not practicable. The variability of pH and manganese content, as well as of other dissolved constituents in stream water, generally requires more sampling and study than are given.

Manganese oxide can be deposited rapidly from solution in the presence of suitable surfaces until a condition of equilibrium as predicted from Eh-pH diagrams is reached (Hem, 1963). Thus, at pH [illegible] manganese would be deposited from aerated water which had more than about 0.10 ppm of manganese in solution. However, at pH 7.2 manganese oxide deposition would not be expected unless the solution contained more than 1.0 ppm. These observations correlate reasonably well with the observed behavior of manganese in ground water. In ground-water aquifers or in water near the bottoms of reservoirs and lakes, which is prevented from circulation by thermal stratification, reducing conditions under which considerable amounts of Mn^{+2} will be stable in solution can be expected. There is little difficulty in finding mechanisms to explain waters having a high manganese content—often, more than one reasonably plausible explanation can be given. The deposition of manganese oxide on the beds of flowing streams is a more difficult process to explain, although some of the instances reported may be due to fairly simple processes.

Ingols and Wilroy (1962) have reported some observations on the manganese content of the Chattahoochee River near Atlanta, Ga. During the summer months, manganese reached high concentrations in the deeper parts of a reservoir in which water was stored for generation of power. As a result, water that was discharged into the river during the late summer and early fall had as much as 15 ppm manganese. The manganese was precipitated as oxide in the riverbed for a few miles below the dam the first year the reservoir was used, but was not carried far downstream in solution. The precipitation of most of the manganese can be readily explained as a result of an increase in Eh and pH of the discharged water as it was aerated by flowing down the river channel. The average pH of the river water at the Atlanta raw-water intake (Lohr and Love, 1952) was reported to be 6.9 during 1950; the maximum observed value was 7.2 and the minimum was 6.5. Evidently the Eh of the river water is sufficiently high for removal of manganese.

It is not unreasonable to postulate that organisms in river water may bring about micro-environments adjacent to or within their structure which attain and maintain higher pH and Eh levels than those of the main water body, and that these growths thereby oxidize the manganese and convert it to MnO_2. This hypothesis has been frequently suggested and, as noted earlier in this report, it was proposed by Ljunggren (1953) as the explanation for manganese oxide deposits on streambeds in southern Sweden.

COPRECIPITATION OF IRON AND MANGANESE

Before concluding that biochemical reactions are the best explanation for all occurrences of manganese precipitates in streams, it should be noted that the manganese oxide precipitates in streambeds often form without obvious indications of biological activity. Certain aspects of manganese chemistry in the presence of iron may be of interest in this connection. Manganese oxide streambed deposits for which analyses are available contain considerable amounts of iron, and iron can be assumed to be present in the water.

In previous work (Hem, 1963), it was shown that when ferric hydroxide was precipitated from a mixed solution of manganous and ferrous ions, the ferrous iron content quickly dropped below detection, and the manganese in solution also decreased although at a slower rate, so long as pH was above 6.5. According to theoretical solubility calculations for pure manganese solutions, no precipitation of manganese should have taken place; hence, the precipitation of iron must have had a considerable influence.

Mixed deposits of manganese and iron oxide in streambeds could perhaps be brought about by coprecipitation, originating on a coating of ferric hydroxide adhering to the surfaces of rocks in the stream. Such an adherent coating would form when the iron was precipitated at a pH low enough to impart a positive electrostatic charge to the particles of ferric hydroxide. A pH below 6.0 would be required for this precipitation of positively charged material, but a considerably higher pH would be required to cause coprecipitation of manganese. In the dilute, poorly buffered water of a stream draining an igneous or metamorphic forested terrane, the necessary pH fluctuations probably could occur. The manganese content of the deposits could be increased at the expense of iron by a replacement process which could take place when the stream characteristics were favorable.

The chemical system in a segment of river where manganese oxide is being deposited is more strongly influenced by oxygen than a ground-water system or the system at the bottom of a lake. In the river segment, the Eh of the water is a function of dissolved oxygen which normally is present in excess and which will not be appreciably affected by oxidation or precipitation reactions involving manganese in solution. The pH, although not constant, is fixed by carbon dioxide equilibria. The amount of ferrous iron in solution will fluctuate in response to pH and Eh. The activity of Fe^{+2}, however, will be a very small fraction of the total amount of iron apparently present. Most of the latter will consist of colloidally dispersed or molecular $Fe(OH)_3$ or complexed forms of ferrous iron. The activity of ferrous ions can be estimated from the pH and Eh (Hem, 1960c) for equilibrium conditions. Biochemical utilization of iron may tend, at times, to depress the ferrous ion activity below the equilibrium value, and any ferrous iron produced by local reactions in the streambed will be carried off by the moving water. One may expect the Fe^{+2} activity in the stream to be at, or possibly at times below, the equilibrium level predictable from the Eh and pH of the water, in the presence of solid $Fe(OH)_3$.

Ferric hydroxide particles have a positive surface charge in water whose pH is low enough, and under these conditions would be attracted to negatively charged surfaces such as those of minerals in a streambed. Once formed, a thin layer of ferric hydroxide might participate in a reaction with manganous ions in the stream water, which can be represented:

$$2\ Fe(OH)_3\ c + Mn^{+2} + 2\ H^{+1} = MnO_2\ c + 4\ H_2O + 2\ Fe^{+2}$$

From the standard free-energy values for the participating substances, the equilibrium constant for this reaction is calculated as $10^{-5.67}$. The reaction is normally displaced to the left—however, when activity of Fe^{+2} is very low and activity of Mn^{+2} is relatively high, some replacement of ferric hydroxide by manganese dioxide will occur.

The negatively charged surface of the MnO_2 would tend to attract more ferric hydroxide, and the process could be repeated to build up a deposit of the two substances. The proportion of manganese to iron would depend on the length of time that conditions were favorable for manganese deposition and on rates of reactions involved.

The mass-law equation for the above reaction

$$\frac{[Fe^{+2}]^2}{[Mn^{+2}]\,[H^{+}]^2} = 10^{-5.67}$$

can be used to calculate equilibrium activities for manganese at various activities of Fe^{+2} and H^{+1}. For example, if $[Fe^{+2}]$ is 10^{-12} molal, at pH 6.5 the solubility of manganese will be $10^{-5.33}$ molar or about 0.26 ppm, and at pH 6.0 the solubility of manganese will be only $10^{-6.33}$ or 0.026 ppm. Thus, if the activity of ferrous iron, which appears as the second power in the equation, can be maintained at a low enough value, the precipitation of manganese can be expected even though the activity of manganese in solution is well below the point where oxide precipitation would be expected when iron is absent (Hem, 1963).

Calculated activity of Fe^{+2} at various pH levels (Hem, 1960c, p. 50) indicates that at pH 6.0 the Eh would have to be +0.69 v, and at pH 6.5, +0.60 v to maintain $[Fe^{+2}]$ at 10^{-12} molal. These Eh values are probably somewhat above levels commonly reached in stream waters but may not be impossible in strongly aerated water in this pH range.

Although Ljunggren (1953) did not obtain Eh measurements, the pH's of streams he studied in Sweden were between 6.2 and 6.8 during one period of summer low flow and generally near or somewhat below 6.0 at higher flow a year later. The amount of manganese in solution was generally less than 0.10 ppm at the low-flow period, but manganese concentrations were not determined in the later observations. The above calculations suggest that coprecipitation may play a part in the deposition of oxides in those streams.

According to Krause (1928), the isoelectric point for ferric hydroxide is at pH 5.2. The observations of the writer (Hem and Skougstad, 1960) suggest that the isoelectric point may be between pH 5.5 and 6.0 in solutions resembling natural water of low dissolved solids concentration. When the pH of the stream water is below the isoelectric point, adherent precipitates of ferric hydroxide may be formed in the bed. Replacement of part of the ferric hydroxide by manganese dioxide will be favored when the water is at a higher pH. This theoretical model obviously needs to be tested by detailed study of a stream in which manganese and iron deposition occurs before it can be verified. Among the kinds of observations needed are accurate measurements of pH and Eh in the precipitation zone, periodic sampling upstream and downstream from the precipitating section to determine seasonal changes in dissolved manganese activity, and detailed examinations of the deposits and the surfaces on which they form to identify any organisms associated with them.

SUMMARY AND CONCLUSIONS

Because manganese oxide deposits can occur in widely differing natural environments, it seems logical to postulate more than one mechanism for their formation. Circulation of manganese from soil to trees and back to the soil by leaf-shedding and similar biochemical mechanisms involving other plant types will tend to leak some soluble manganese, both to surface runoff and to ground water. Biochemical processes probably are frequently associated with both the solution and the deposition of manganese, where energy relationships are favorable for the organisms that participate.

The oxidation of manganous ions in aerated water is very slow at near-neutral pH, but the oxidation rate can be increased by inorganic catalysis. Many of the mineral surfaces to which natural water is exposed have some cation-exchange sites, which may strongly attract manganese ions. The surfaces of feldspathic sand grains, for example, adsorb manganese, and when they are saturated with adsorbed manganese ions, the surfaces catalyze the oxidation process.

Coprecipitation of manganese oxide and ferric hydroxide can take place in aerated water whose pH is below 7.0, if ferrous iron activity is kept low. Such a process may be important in the deposition of mixed oxides in streams and lakes.

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