Relation of Electrochemical Potentials and Iron Content to Ground-Water Flow Patterns

GEOLOGICAL SURVEY PROFESSIONAL PAPER 498-C
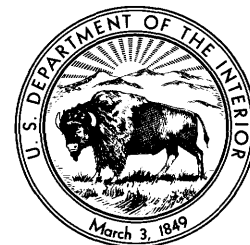
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By WILLIAM BACK *and* IVAN BARNES

HYDROLOGY OF AQUIFER SYSTEMS

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Explains the reasons for the distribution and concentration of iron in ground water and summarizes the methods of making the field measurements and interpreting the results

UNITED STATES DEPARTMENT OF THE INTERIOR

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RELATION OF ELECTROCHEMICAL POTENTIALS AND IRON CONTENT TO GROUND-WATER FLOW PATTERNS

By WILLIAM BACK and IVAN BARNES

ABSTRACT

This study was undertaken to develop means of measuring oxidation potentials in aquifer systems and to use the measured values in interpreting the behavior of iron in ground water. Anne Arundel County, Md., was selected as the area of study because of the wide range of concentration of iron—nearly zero to about 35 ppm—in the ground water and the rather complete information on the geology and hydrology. The regional geology consists of coastal plain sediments ranging in age from Early Cretaceous through the Recent. Most of the pH and oxidation-potential measurements were made in nonmarine Cretaceous deposits, only a few in the marine Eocene. Iron-bearing minerals in the area are primarily hematite or limonite and glauconite with a small amount of pyrite.

Equipment was developed that permits the measurement of oxidation potentials by use of saturated calomel and platinum electrodes in ground-water samples uncontaminated by oxygen of the atmosphere. Measured Eh values range from about +700 mv to −40 mv. Approximately 2 to 3 hours are required to measure a stable or nearly stable oxidation potential.

The mineralogy and organic content of the deposits and the ground-water flow pattern are the primary controls on the oxidation potential and pH of the water. A correlation exists between the oxidation potential and the concentration of iron in ground water; the higher concentrations occur in waters with the lowest values of Eh. The concentration of iron in the water tested shows little correlation with the pH of the water. The highest oxidation potentials were measured in water produced from shallow wells and those wells in recharge areas. The lowest potentials were measured farthest downgradient in water associated with gray and green sediments. The Eh values measured in the field are between values predicted from the solubility of $Fe(OH)_3(c)$ and values predicted from the solubility of hematite.

INTRODUCTION

Many ground-water geologists have observed the results of chemical reactions between water and various forms of iron. One of the most common observations is the rusty discoloration of a water sample that was clear when collected. Another observation frequently reported in ground-water literature is the wide range in concentration of iron and its sporadic distribution within a single aquifer. For example, Winslow and others (1953, p. 112) show concentration of iron, which ranges from 0.14 to 5.7 ppm, in glacial drift in Cuyahoga County, Ohio. Parker and others (1955, p. 788) give a range of concentration of iron between 0.12 to 8.8 ppm for the nonartesian aquifer in the Miami metropolitan area. Cederstrom, Trainer and Waller (1964) show the occurrence of iron ranging from 0.00 to 11 ppm in the shallow aquifer near Anchorage, Alaska. Back (1957, p. 56) shows that iron concentration in water from flood-plain deposits along Smith River, California ranges from 0 to 9.7 ppm. Acid waters draining coal mines in Kentucky and Pennsylvania have iron in solution ranging up to hundreds of ppm. Although these examples represent different hydrologic environments and geologic terranes, each area reportedly contains organic or inorganic oxidizable material. In addition to organic material, coal mines commonly contain such oxidizable inorganic material as pyrite and marcasite.

Other observations of reactions between iron and water are (1) corrosion of well casings, (2) plugging of screens and distribution systems with rusty precipitates, (3) formation of "iron hard-pans" a few feet below land surface.

This study was directed toward the description and interpretation of field observations that would assist in understanding such phenomena as those mentioned and to determine if oxidation potentials can be measured in ground water to aid in understanding the behavior of those ionic species which exist in more than one oxidation state. An area was selected in which the water has a wide range of iron concentration. The specific objective of this study was threefold: the first objective was to develop equipment and techniques to measure oxidation potentials in ground water; the second was to relate the potentials to the flow pattern of the water and the occurrence of iron in the water; and the third was to determine if the measured potentials can be used with established electrochemical theory to explain the concentration and valence state of iron in the water. The first and third objectives have been dis-

cussed in separate papers (Back and Barnes, 1961; Barnes and Back, 1964).

We greatly appreciate the assistance and access to the wells given by the many well owners in the area. In particular we are grateful for the cooperation received from Mr. L. V. Booker, of Anne Arundel County, Sanitary Commission; Mr. Robert Davis, U.S. Naval Academy; Mr. F. V. Leitch, Annapolis City Water Works; Mr. Robert Irving, Crownsville State Hospital; and Mr. Albert M. Tawney, (deceased, 1962) Post Engineers Office, Fort Meade, Md.

We express our thanks to our many colleagues who provided assistance during this study, in particular to F. K. Mack for making available stratigraphic correlations and water-level maps; to P. R. Seaber and H. B. Wilder for their help in making many of the measurements in the field; and to Bruce B. Hanshaw for his review of the manuscript.

THEORETICAL BACKGROUND AND TECHNIQUES

The concept of oxidation-reduction potentials—also called redox potentials, Eh or ORP—has been used in numerous applications. For example, the work of Pourbaix (1949; see also Garrels, 1960, p. 197–199 for list of Technical Reports of the Belgian Center for study of corrosion) has been directed toward studies of corrosion of metals. Evans and Garrels (1958) and James (1954) have applied the principles of redox potentials and pH to the interpretation of geochemical phenomena in geologic systems.

An extensive literature exists dating from the early nineteen thirties describing attempts by limnologists and oceanographers (ZoBell, 1946) to interpret redox potentials and pH in natural systems. Knowledge of oxidation potentials is becoming increasingly important in developing the technique for the removal of constituents such as manganese (Adams, 1960) and iron (Weart and Margrave, 1957) from public water supplies. Henry (1960) has described equipment and techniques he has developed to measure oxidation potentials in sewage to determine the amount of aeration and chlorination required. Baas Becking and others, (1959) have summarized about 5,200 pH and Eh measurements made in natural environments. About a hundred of these measurements are of ground water; most of the samples were collected from springs. It is not reported how the measurements on spring waters were made and it is possible that the reported oxidation potentials are higher than the true Eh value owing to contamination by the oxygen in the atmosphere.

The only previous attempts known to the writers to measure the oxidation potential of ground water in such manner as to prevent the contamination of the sample

by the oxygen are by Germanov and others (1959), by Sato and Mooney (1960), and by Sato (1960). The samples were collected from flowing bore holes drilled from the land surface or from holes drilled in underground mine workings. We know of no studies in which oxidation potentials have been measured in ground water produced from pumping wells.

The electrochemical background on which this study is based is summarized in several places (Garrels, 1960, p. 12–20; Sato and Mooney, 1960, p. 230–231). These discussions follow Pourbaix (1952) and Latimer (1952; 1957). Electrochemical reactions that are both Eh and pH dependent in an aqueous medium can be expressed in the general form,

$$aA + wH_2O = bB + mH^+ + ne^-$$
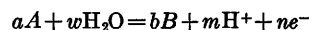
where a and b represent the number of moles of A and B respectively, w is the number of moles of water, m is the number of moles of hydrogen ion, and n is the number of electrons, e, released in the reaction. The species on right side of the reaction are in the oxidized state. Some reactions are independent of pH or Eh, in which case m or n is zero. The Nernst equation, which may serve as a definition of Eh, states:

$$Eh = E° + \frac{RT}{nF} \ln \frac{[B]^b[H^+]^m}{[A]^a[H_2O]^w}$$

where Eh is the potential referred to the hydrogen electrode, $E°$ is the potential of the reaction when all species involved are at unit activity and is temperature dependent, R is the gas constant, T the absolute temperature in degrees Kelvin, and F the Faraday, an electrical constant. Brackets denote activity or thermodynamic concentration. Remembering that pH is the negative logarithm of the hydrogen ion activity, the significant variables become temperature, Eh, pH, and the activities of the ions under consideration.

Fields of stability for various forms of iron occurring in natural waters are shown in figure 1. Note that $Fe(OH)_3(c)$ and $Fe(OH)_2(c)$ are crystalline forms, whereas the others are ionic species. Dissolved species are often indicated by (aq) and solid phase by (c).

To measure the oxidation potential, water was withdrawn by a valve attached to the discharge pipe, flowed through plastic tubing into a sealed measuring chamber containing electrodes (fig. 2) and discharged through 15 feet of plastic tubing. The sampling procedure involves prolonged flushing of the measuring chamber. The volume of the chamber is about 275 ml and the rate of flow was about 30 ml per second. It is assumed that after an hour of flushing, contamination by water and air initially present in the sample jar is not a serious problem. A detailed description of the

equipment and sampling methods is described by Back and Barnes (1961).

Electrical potentials were measured between the saturated calomel electrode (sce) and a noble-metal elec-

FIGURE 1.—Stability-field diagram for aqueous ferric-ferrous system. Adapted from Hem and Copper, 1959.

FIGURE 2.—Equipment used to measure oxidation potentials.

trode, either platinum or gold. The noble-metal electrodes are electrical contacts only, and take no part in any chemical reaction, except as catalysts. For iron, as an example, an oxidation reaction may be written

$$Fe^{+2} = Fe^{+3} + e^- \tag{6}$$

where e^- is the electron lost or gained by the electrode as the reaction proceeds to the right or left. The measured potential is the difference in potential between the platinum or gold electrode and the saturated calomel electrode. The measured potentials are converted to Eh by adding the potential of the saturated calomel electrode obtained from the following equation

$$E°_{(sce)} = +0.2415 - (0.00076)(T-25)$$

where T is in degrees centigrade.

The Eh-time curves have either a negative slope, which is more common, or a positive slope (Barnes and Back, 1964). In all cases the rate of change of the potential was greatest during the early part of the sampling period. After the potential became steady, the sample was considered representative and the flow was stopped. The criterion for a steady potential was less than 1 mv change during a 5-minute time interval at a constant flow rate. The true value of the potential was assumed to be the highest potential for a static sample for curves with positive slopes or the lowest value for curves with negative slopes. The static potentials were reproducible to within 10 mv in any one sampling period.

It may be noted that in tables 2 through 5 potentials are different for the platinum and gold electrodes. The gold versus sce potentials are low in comparison with plantinum versus sce when measured in water of high redox potential, and tend to be high relative to platinum in waters of low redox potential. The potentials with the gold electrode were not interpreted and only the potentials obtained with the platinum electrode were used on the illustrations and in the calculations for this study.

A pH glass electrode was used to measure hydrogen ion activity. The potential of a pH electrode measured against the sce is a function of the thermodynamic concentration (activity) of hydrogen ions in solution.

Samples of water were collected for iron analyses in the laboratory. Ferrous iron can be preserved in aerated water for about 2 days by complexing the ferrous iron. An aqueous solution of 0.2 percent 2.2′-bipyridine was used in the proportion of 1 ml per 25 ml of sample. The ground water was added to the complexing solution, and thoroughly mixed to prevent aeration before complexing. If the color was more intense than pale pink the sample was diluted 1:10 or
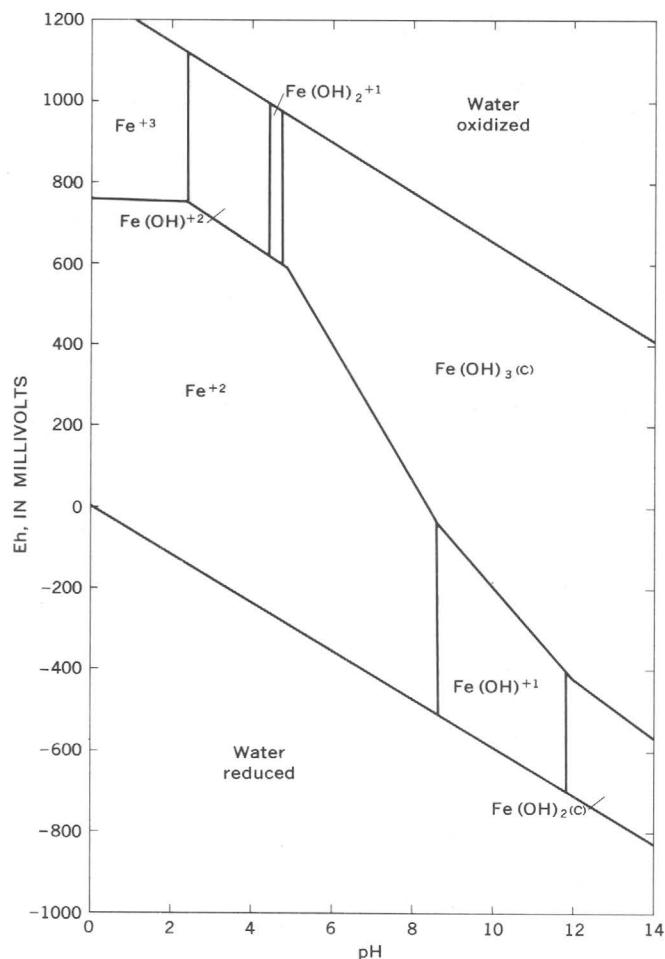
1:20 with deionized water. The samples were taken to the laboratory and analyzed within 48 hours after collection.

GEOLOGIC AND HYDROLOGIC CONDITIONS IN ANNE ARUNDEL COUNTY, MD.

Anne Arundel County, in the northeastern part of southern Maryland along the west side of Chesapeake Bay, was selected as the study area because the wide range of concentration of iron permits correlation with the hydrologic environment, the mineralogic character of the sediments is relatively simple, and the regional geology and hydrology are well known. The existence of a number of high-capacity deep wells permitted sampling of water with a minimum chance of contamination of the sample. The generalized geology of the area, location of wells and the lines of profiles for the fence diagrams are shown in figure 3.

Anne Arundel County is almost entirely within the Coastal Plain Province in which the upland is flat to gently rolling. The surface is sharply dissected in many coastal areas by tributaries of numerous estuaries. The altitude ranges from sea level to more than 200 feet. The undissected areas of higher altitudes are generally the ground-water recharge areas, and the topographic lows coincide with piezometric lows which are ground-water discharge areas.

Bennett and Meyer (1952, p. 41) conclude that part of the Patuxent Formation (table 1 and fig. 3) was formed by large coalescing alluvial fans from the high crystalline-rock area west of the Fall Zone. The alluvial fans probably merged eastward with sediments deposited in an environment characterized by numerous streams channels and associated flood plains containing lakes and swamps. The sediments of the Arundel Formation are of continental origin and presumably were deposited in swamps. The Arundel Formation is a confining bed for the underlying Patuxent Formation, but may not be impermeable enough to prevent movement of some water between the underlying Patuxent and the overlying Patapsco Formation.

A slight elevation of the area after deposition of the Arundel Formation recreated conditions similar to the environment during Patuxent time that permitted deposition of the Patapsco sediments which are lithologically similar to those of the Patuxent.

A subsequent slight encroachment of the ocean on an eroded surface of low relief caused the sediments of the Raritan and Magothy Formations to be deposited in an environment transitional between continental and marine. The Raritan and Magothy deposits are fluviatile, estuarine, or deltaic.

TABLE 1.—*Stratigraphic units in Anne Arundel County, Md.*

Age	Formation and symbol	Thickness (feet)	Lithology	Origin	Iron-bearing minerals
Pleistocene and Pliocene.	Q	0–40	Gravel, sand silt and clay.	Marine terraces and fluviatile deposits.	Limonite.
Miocene	Calvert (Tc)	100–150	Sandy clay, diatomaceous earth layer, silt, shell beds.	Nearshore marine	Do.
Eocene	Nanjemoy (Tn)	75–120	Sand and clay	Marine	Glauconite.
	Aquia (Ta)	75–120	Sand	do	Do.
Paleocene	Brightseat [1]			do	Glauconite, limonite.
Cretaceous	Monmouth (Kmo)	50–80	Sandy clay	do	Glauconite.
	Matawan (Kma)	50±	do	do	Do.
	Magothy (Km)	25–60	Sand and clay; abundant lignite.	Estuarine and deltaic	Pyrite, small amount of limonite.
	Raritan (Kr)	100±	Sand	Fluviatile and estuarine.	Limonite.
	Patapsco (Kpa)	100–300+	Clay and sand	Fluviatile	Do.
	Arundel (Ka)	25–200	Clay	Swamp	Nodules of limonite.
	Patuxent (Kpx)	100–300+	Sand, clay gravel	Fluviatile	Limonite.
Pre-Cretaceous	pK		Metamorphic and igneous rocks.		

[1] Not identified in Anne Arundel County. Probably occurs in southern part of County.
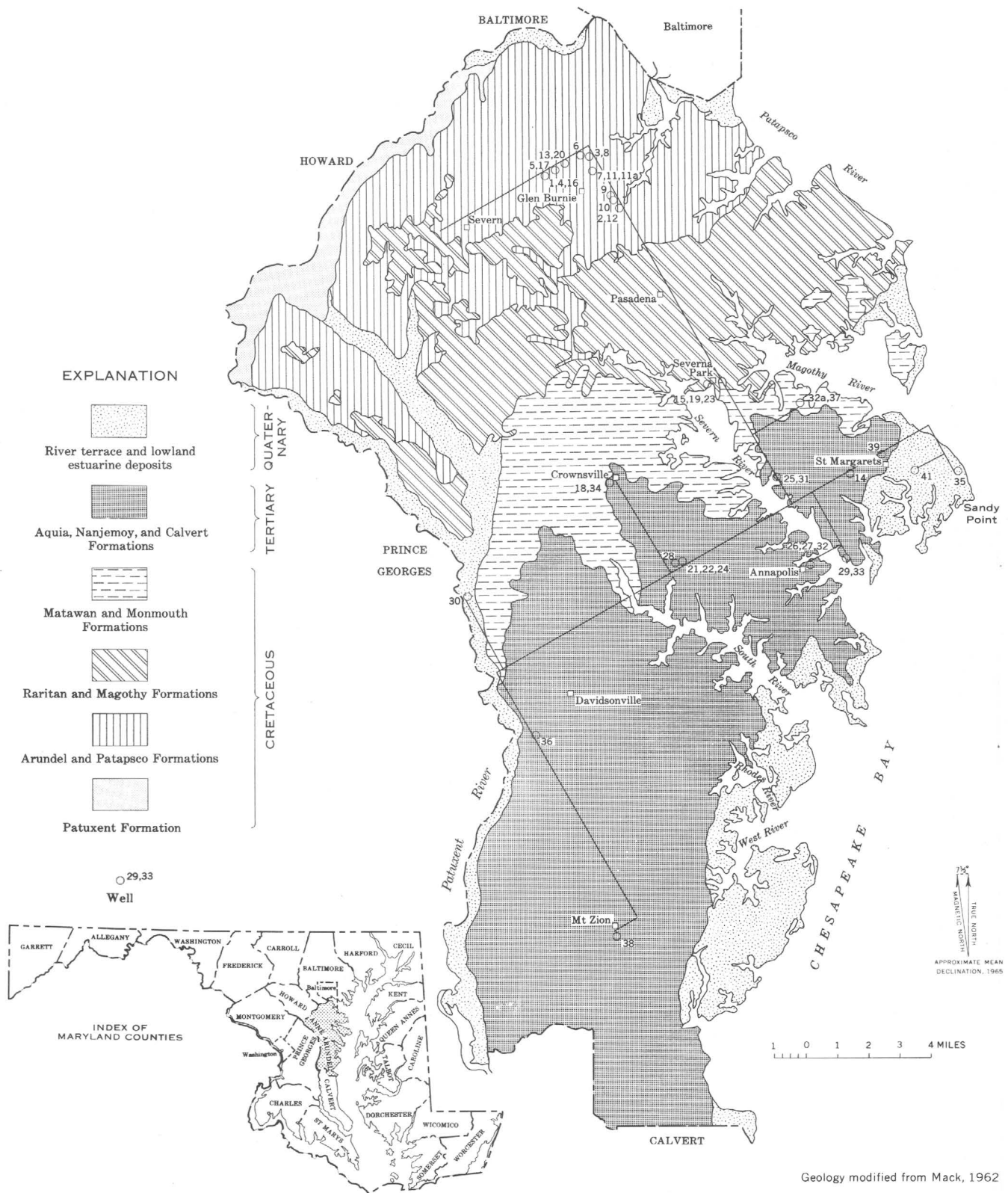
FIGURE 3.—Generalized geologic map of Anne Arundel County, Md., showing location of wells and profiles used for fence diagrams.

The continuing encroachment of the sea caused the deposition of the Matawan and Monmouth sediments in a marine environment. Glauconite does not occur below the Magothy but is abundant to common from above the Magothy to the base of the Miocene. The Matawan and Monmouth Formations contain deep-green botryoidal and oolitic glauconite indicative of marine conditions. Near the outcrops some hematite is found as pseudomorphs after glauconite.

The marine Brightseat Formation of Paleocene age has not been identified in Anne Arundel County. Judging from its thickness and attitude in adjacent areas, it is probably present in the southern part of the county. For the purposes of this report the sediments equivalent to the Brightseat Formation are included in the Monmouth Formation.

The marine Aquia Greensand of Eocene age overlies the Cretaceous sediments and is composed chiefly of fine to coarse green glauconitic argillaceous sand. In the outcrop the Aquia Greensand weathers to dark brown sand and sandy clay. The overlying Nanjemoy Formation consists largely of green glauconitic sand and some gray clay; the basal part consists of a dense, even textured, pink to gray clay member that confines the water in the Aquia Greensand.

The Calvert Formation of Miocene age, unconformably overlying the Nanjemoy Formation, is a sandy clay with associated diatomaceous layers. The Pleistocene deposits, consisting of sand and gravel, overlie many of the formations in the area; the sediments are commonly stained with limonite or hematite.

The fence diagrams (pls. 1, 2, and 3) show the generalized ground-water flow pattern and the stratigraphy. The salient features of these sediments, which are predominantly clastic, are (1) the relatively high abundance of limonite in the lower formations through the Patapsco, (2) a decreasing amount of limonite in the Raritan and Magothy, (3) its absence in the Matawan and Monmouth Formations and a small amount in the overlying Tertiary sediments, and (4) the abundance of limonite in the Pliocene and Pleistocene sediments. Samples of sediments from well cuttings were examined with binocular microscope and the presence of iron oxides was noted. No attempt was made to differentiate between limonite and hematite and the material is referred to in this report as limonite.

The generalized direction of movement of the ground water shown on the fence diagrams was constructed from an interpretation of the piezometric maps, figures 4 through 7. The piezometric surfaces of the four major aquifers, the Patuxent, Patapsco, Raritan and Magothy, and Aquia are shown on figures 4 through 7, respectively.

The head of water in the Patuxent Formation shows a range from about 140 feet above sea level to 40 below sea level. Most of the water enters the formation in the topographically high areas along the west county line and flows in an easterly and northeasterly direction and is discharged by pumping in the industrial area of Baltimore.

The head of water in the Patapsco Formation (fig. 5) ranges from about 100 feet above sea level to sea level. Much of the water enters the formation in the outcrop area which strikes northeasterly across the county. The water flows generally in an easterly and southeasterly direction. A piezometric high in the Patapsco Formation near Pasadena resulting in part from higher topography causes part of the water to flow toward the north and west, and part to be discharged into local estuaries.

The outcrops of the Raritan and Magothy Formations strike across Anne Arundel County. These formations are recharged in part within the outcrop area that extends southwestward through Prince Georges and Charles Counties. The head in the Raritan and Magothy Formations (fig. 6) is generally higher than the head in the Patapsco and Patuxent Formations. For most of the area shown on the fence diagrams this means the water can move downward from the Raritan and Magothy Formations into the Patapsco and Patuxent Formations. The piezometric high on the peninsula near St. Margarets causes the water to be discharged in all directions toward the estuaries and Chesapeake Bay. The topographically low area near Severna Park, between the estuaries of the Severn and Magothy Rivers, is a major discharge area for the Raritan and Magothy Formations. The small closed contour west of Annapolis results from pumping in the Annapolis city well field.

The piezometric surface for the Aquia formation is shown for the southern part of the area (fig. 7). The Aquia formation is recharged from the adjoining counties to the west and along the outcrop that extends northeasterly across Anne Arundel county. Some of this water is discharged into Chesapeake Bay and some into the Patuxent River to the west of Mt. Zion. Equal-value contours for the piezometric surface of water in the Raritan and Magothy Formations and in the Aquia Greensand cross in several places. This may indicate a complex hydrologic relationship between these two aquifers. In part of the area shown on the fence diagram (pl. 1) between Davidsonville and Mt. Zion, the water may be moving downward from the Aquia into the Raritan and Magothy Formations and in other places the reverse may be true. Near Mt. Zion the water in the Raritan and Magothy Formations is moving generally in an easterly direction; in the Aquia the water
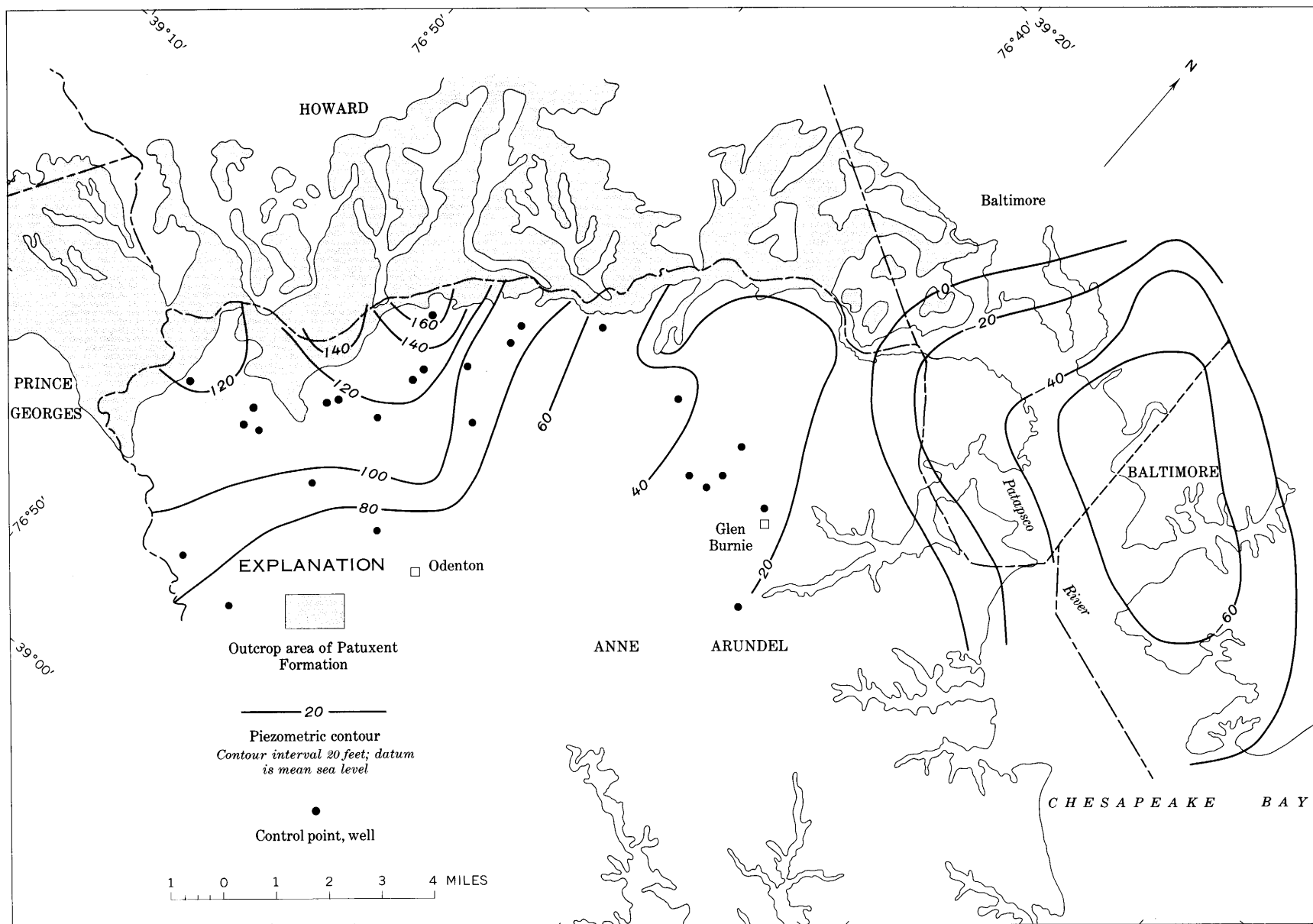
FIGURE 4.—Map showing outcrop and the piezometric surface of the Patuxent Formation. Adapted from Mack, 1962.
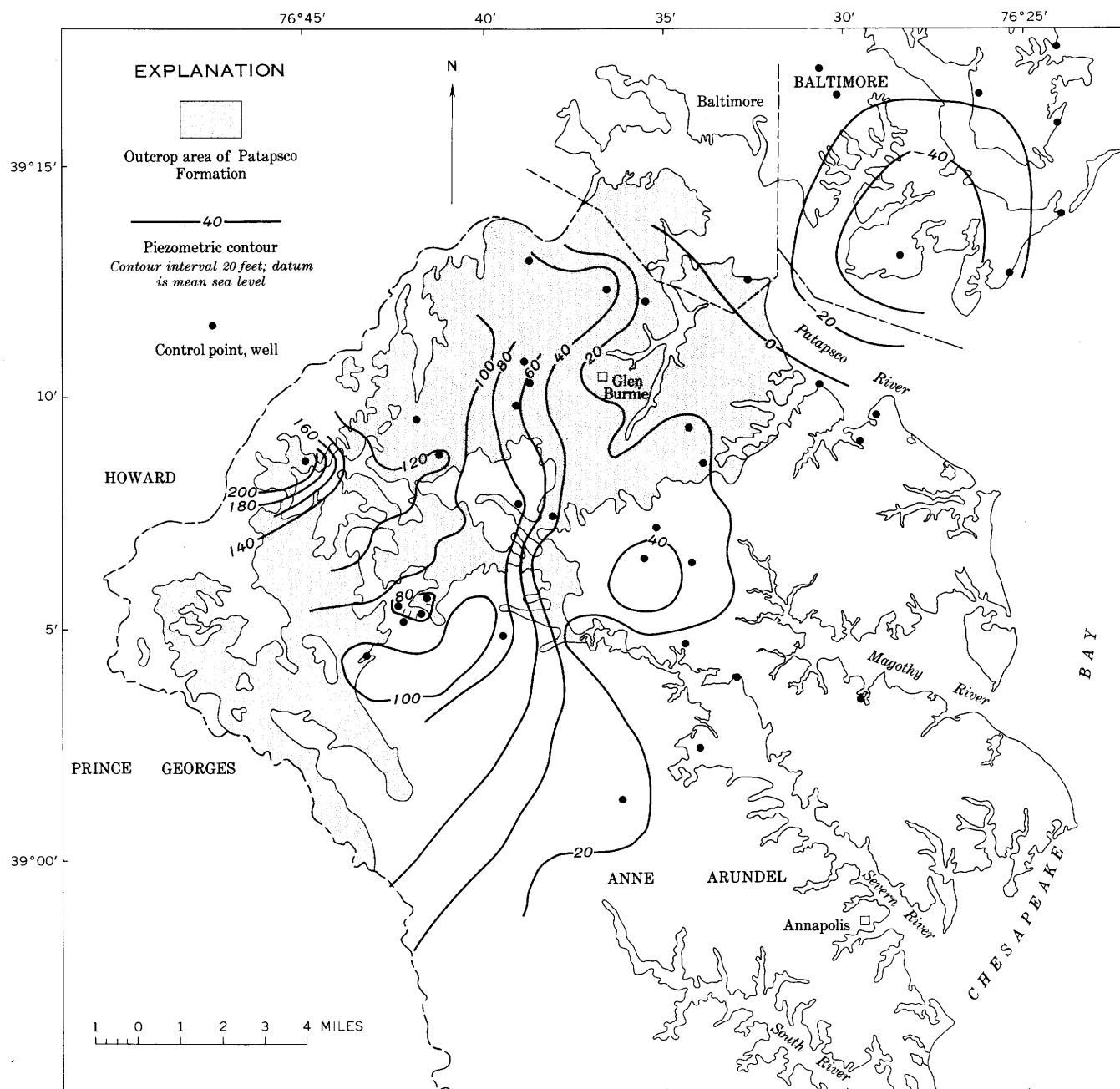
FIGURE 5.—Map showing outcrop and the piezometric surface of the Patapsco Formation. Adapted from Mack, 1962.

is moving in a westerly direction. The discharge from the Aquia Greensand produces the piezometric low area along the entrenchment of the Patuxent River.

RELATION OF Eh, pH, AND IRON CONCENTRATION TO HYDROLOGY

A brief description of the wells and a summary of the field and laboratory measurements are given in table 2. The description of the wells, altitude, depth, yield, and water-level measurements were obtained from Brookhart and Bennion (1949), Otton (1955), and Mack

(1962). Field measurements used in the calculations and in preparation of the illustrations in this report were made during November and December 1960, and January and February 1961.

The stratigraphic and geographic distribution of the oxidation potentials, pH, and iron concentration are shown respectively on plates 1, 2 and 3. The values are plotted at the location of the bottom of the well. The wells are projected less than a mile to the cross sections. Iron values are expressed in molality in plate 3. A molal concentration of 10^{-3} equals the atomic weight of
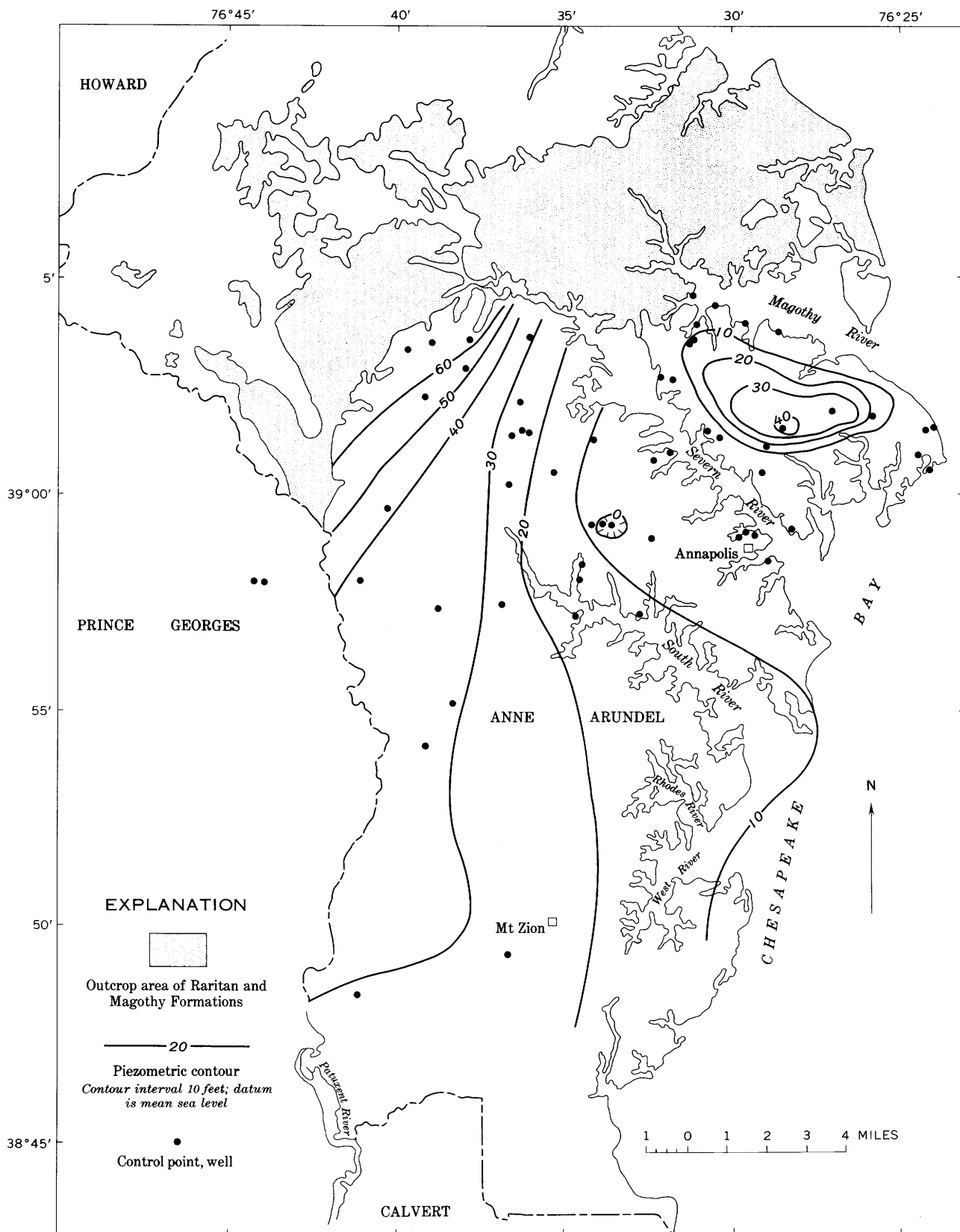
FIGURE 6.—Map showing outcrop and the piezometric surface of the Raritan and Magothy Formations. Adapted from Mack, 1962.
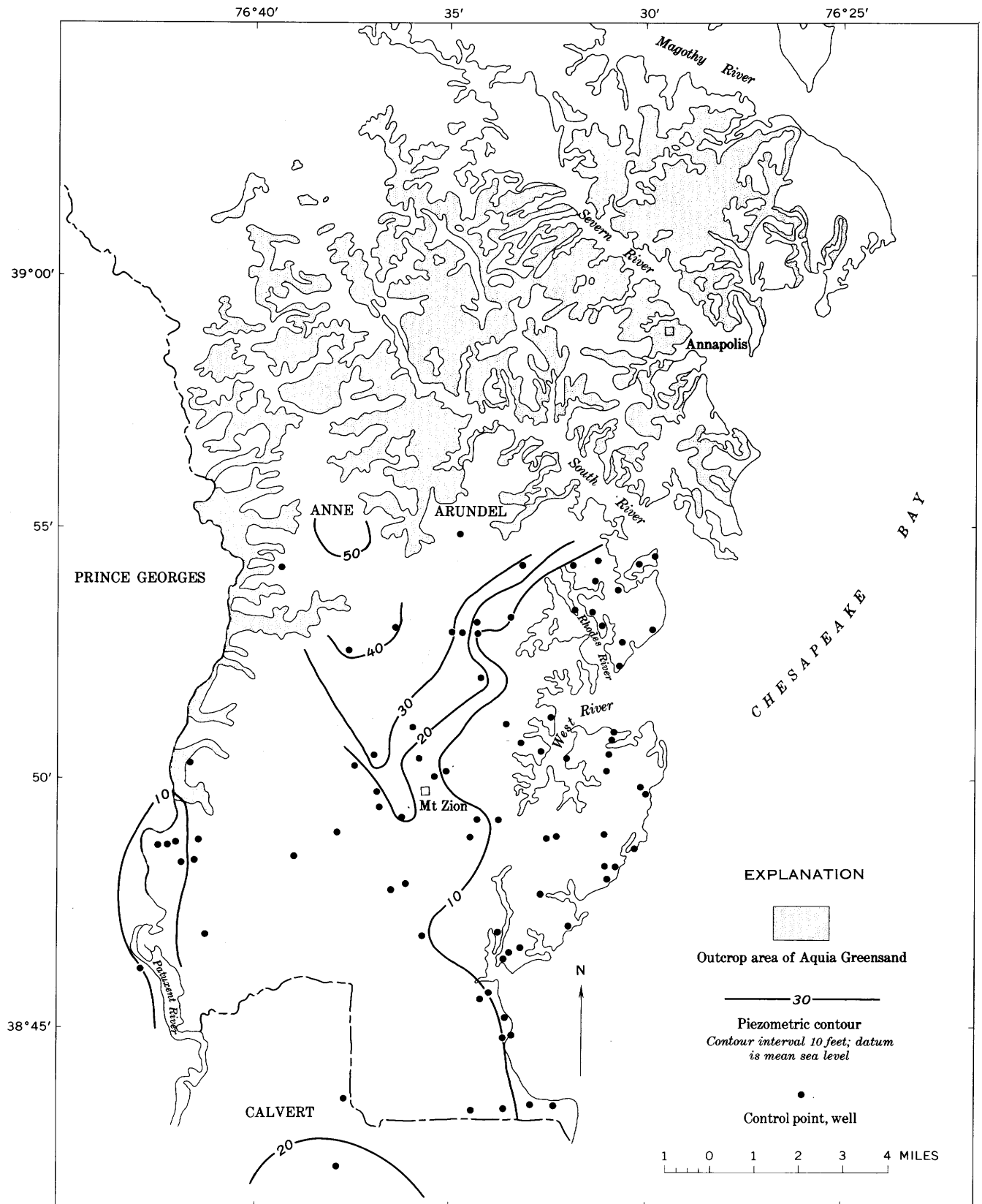
FIGURE 7.—Map showing outcrop and the piezometric surface of the Aquia Greensand.   Adapted from Mack, 1962.

the element expressed in parts per million—that is, an iron concentration of 10^{-3} molal equals 55.8 ppm and 10^{-6} molal equals 0.05 ppm. The limit of detection is about 0.009 ppm.

PATUXENT FORMATION

Hydrologic and chemical data are given in table 2 for wells producing from the Patuxent Formation. The oxidation potential ranges from about 350 to 450 mv, which is approximately 300 mv lower than the Eh of water from the overlying Patapsco Formation in the Glen Burnie area (pl. 1). As shown of plate 1 the potential of the water decreases as the water moves downward from the Patapsco Formation to the Patuxent Formation. Lowering of the potential causes an increase in the iron content as shown in (pl. 3). The pH of the water from both aquifers is about 4.5 in this area (pl. 2).

PATAPSCO FORMATION

Data for wells producing from the Patapsco Formation are given in table 2. This aquifer produces water under various hydrologic conditions and as a result the oxidation potentials range widely, from 145 to 700 mv. The wells from the Glen Burnie area have the highest potentials (654 to 701 mv) measured during this study (pl. 1). This part of the formation is primarily a recharge area within which the water moves downward from the surface and laterally through the sediments generally southeasterly toward Annapolis. The oxidation potentials gradually decrease in the direction of water movement.

Farther downdip and downgradient on the piezometric surface of the Patapsco Formation, wells near Severna Park (Nos. 15, 19, 23) produce water that has been recharged through the Raritan and Magothy Formations. This water has lower potential (243 to 471 mv) than that from the Patapsco in the Glen Burnie area (pl. 1).

Wells producing water from the Patapsco (Nos. 26, 27, 29, 31 and 33) with the lowest potentials from that formation (145 to 214 mv) are near Annapolis. Most of this water may be moving upward to the well screens from greater depths (pl. 1). This low potential combined with a fairly low pH of 5 to 6 (pl. 2) causes about 20 ppm of iron (pl. 3) to be in solution.

Well 32a produces water from the Patapsco Formation in an area where a piezometric high exists in the Raritan and Magothy Formations. The low potential of 153 mv may be caused by the water moving downward through the lignite-bearing beds of the Raritan. Oxidation of organic material and sediments which contain ferrous iron lowers the potential of the water. The

pH of 3.4 is exceptionally low; the iron content is 8 ppm.

RARITAN AND MAGOTHY FORMATIONS

Data for wells that produce water from the Raritan and Magothy formation are given in table 2. The stable potentials of this water are among the lowest measured, ranging from −20 to +384 mv. These formations contain lignite and ferrous iron as indicated by the grey and green color of the clay. The overlying marine sediments contain abundant glauconite. The lowest potentials (wells 35, 37, 39 and 41) are related to the piezometric high of this aquifer northeast of Annapolis. We believe the oxidation of lignite causes the potential to be low. The high head and small amount of pumping prevents mixing of water from the underlying Patapsco Formation which has slightly higher potential (pl. 1).

As shown on plate 1 the wells west of Annapolis, at the city well field, have slightly higher oxidation potentials that may result from mixing of Patapsco water owing to the relatively low head in the Raritan and Magothy formations.

The difference in potential of more than 250 mv between wells 18 and 34 is unexplained. These wells are of about the same depth and produce water from near the outcrop through which the aquifer is recharged. The pH of 3.6 and 3.2 is extremely low; the iron content is about 2.0 ppm.

AQUIA GREENSAND

Data for wells that produce from the Aquia Greensand are given in table 2. The water from the Aquia shows a wide range of potentials: −13, 55, and 582 mv.

Well 14 is in an outcrop area of the Aquia that serves to recharge much of the formation. The potential of this water was 582 mv (pl. 1), among the highest measured. The pH is 5.5 and the iron content about 0.5 ppm. The water produced here is moving downward from the land surface and has been in contact with no iron mineral other than fresh and weathered glauconite.

The water produced from the Aquia Greensand by well 38 has flowed downgradient from the piezometric high area near Davidsonville toward the discharge area along the Patuxent River. Some water produced from this well has moved vertically upward from the Raritan and Magothy Formations. This water, therefore, has been in contact with glauconite and pyrite, and has one of the lowest oxidation potentials measured (55 mv) and one of the highest pH values (7.42) measured. The values for well 40, a few miles southwest of Mt. Zion, are not shown in the fence diagrams. Its stable potential was −13 mv with pH of 7.8 and 0.48 ppm iron.

TABLE 2.—Description of wells and chemical data for water from the Patuxent, Patapsco, Raritan, and Magorthy Formations and the Aquia Greensand

[AACSC, Anne Arundel County Sanitary Commission; AWW, Annapolis water works]

Index No.	Owner and location	USGS No.	Altitude (feet)	Depth of well (feet)	Depth of casing (feet)	Screen setting (interval in feet)	Water level Date	Water level Depth (feet)	Yield (gpm)	Date of measurement	pH Field	pH Lab	Fe++ (ppm)	Fe+++ (ppm)	Pt vs. SCE	Eh	Au vs. SCE	Temperature (° C)
						Patuxent Formation												
16	AACSC Dorsey Rd., No. 13	Bd 66	85	517	497	497-517	10-31-57	31	375	12- 1-60	4.48	4.6	0.29	0.09	+220	+455	+180	15.5
17	AACSC Dorsey Rd., No. 5	Ad 76	66	474	449	449-474	11-57	34.5	450	11-29-60	4.55		.60	.07	+162	+397	+5	15.6
20	AACSC Dorsey Rd., No. 2	Bd 57	68	510	485	485-510	1-13-56	12	475	12- 1-60	4.80	4.8	.91	.10	+110	+345	+13	15.7
						Patapsco Formation												
1	AACSC No. 4	Ad 74	87	186	171	171-186	10-57	33	375	11-29-60	5.01		0.00	0.03	+468	+701	+90	14.3
2	AACSC Harundale, No. 3	Bd 63	20	180	160	160-180	9- 9-55	0	500	12- 7-60	5.00	5.10	.00	.01	+462	+695	+91	13.5
3	AACSC Glen Burnie, No. 4	Ad 40	55	102		80-102	4- 9-47	28	275	12- 6-60	4.97	5.10	.00	.01	455	+688	+170	14.0
4	AACSC Dorsey Rd., No. 1	Bd 55	70	131	111	111-121	12- 6-55	11	400	11-29-60	5.08		.00	.05	+453	+686	+102	13.8
5	AACSC Dorsey Rd., No. 3	Bd 56	62	153	133	133-153	2- 8-56	7	350	11-29-60	4.96		.00	.01	+452	+685	+128	13.5
6	AACSC Glen Burnie, No. 7	Ad 68	50	160	140	140-160	12-11-53	16	400	12- 6-60	5.00	5.10	.05	.02	+450	+684	+203	14.5
7	AACSC Glen Burnie, No. 5	Ad 41	45	153	126	126-146	6- 4-47	10	250	12- 6-60	5.01	5.10	.00	.00	+450	+683	+120	13.7
8	AACSC Glen Burnie, No. 6	Ad 67	40	151	131	131-151	11-18-53	12	487	12- 6-60	5.03	5.20	.00	.01	+445	+678	+129	13.5
9	AACSC Harundale, No. 1	Bd 36	30	123	98	98-123	7- 3-51	3	439	12- 8-60	4.90	5.2	.00	.02	+442	+675		13.6
10	AACSC Harundale, No. 4	Bd 61	40	206	186	186-206	8- 2-55	13	500	12- 8-60	4.90	5.4	.00	.00	+442	+674		13.0
11	AACSC Glen Burnie, No. 1	Ad 1	45	65			1943	Flowing	225	12- 7-60	4.87	5.05	.00	.01	+440	+673	+140	13.7
11a	AACSC Glen Burnie, No. 3	Ad 23	45	100		63- 73			150	12- 7-60	4.80	5.00	.00	.01	+430	+663	+235	13.5
12	AACSC Harundale, No. 2	Bd 37	20	115	90	90-115			450	12- 7-60	4.77	5.1	.00	.01	+422	+654		13.0
13	AACSC, Dorsey Rd., No. 11	Bd 64	73	181	161	161-181	9-12-57	13	375	12- 1-60	4.92	5.1	.00	.01	+385	+618	+218	13.5
15	AACSC, Severna Park, No. 2	Ce 67	10	185		175-185	8-19-54	1	174	12- 9-60	3.91	4.0	1.4	.06	+238	+471	-109	13.5
19	AACSC, Severna Park, No. 2	Ce 66	10	119	109	109-119	1950	Flowing	155	12- 9-60	4.04	4.0	1.5	.07	+143	+375		13.4
23	AACSC, Severna Park, No. 3	Ce 65	10	150	130	130-150	7-30-59	1	300	1-13-61	4.08	3.8	1.3	.35	+10	+243	-50	13.7
26	U.S. Naval Acad., No. 11	Df 12	10	600		426-493	1-39	2	1,000	11-28-60	6.10		20	.38	-21	-214	-21	16.8
27	U.S. Naval Acad., No. 12	Df 13	14	600		518-588			920	11-30-60	6.05	4.4	18	1.6	-45	+190	-28	16.2
29	U.S. Exp. Sta. No. 3 on Hill	Df 64	32	402		350-402		65	650	12- 8-60	6.05	5.5	17.2	1.00	-50	+185	-58	16.5
31	AACSC Pines, No. 1	Ce 70	15	416	396	396-416	1959	10	450	11-30-60	5.04	4.4	16	1.1	-70	+164	-16	15.0
32a	AACSC, Belvedere, No. 1	Cf 62	58	325	310	310-325	4-15-54	63	150	1-13-61	3.43	3.6	8.0	.71	-80	+153	-40	14.4
33	U.S. Exp. Sta. No. 2	Df 16	10	600		483-600	1946	+11.9	620	1-11-61	5.06	3.9	19	.82	-90	+145	-170	16.8
37	AACSC, Belvedere, No. 2	Cf 64	65	332	312	312-332	10-15-56	54	465	1-13-61	4.92	4.6	9.7	1.6	-151	+82	-60	14.3
						Raritan and Magothy Formations												
18	Crownsville State Hosp., No. 4	Cd 50	131	276	249	249-276	3-12-61	107.8	415	1-12-61	3.66	3.9	1.3	0.51	+151	+384	-6	13.5
21	AWW No. 6, near reservoir	De 45	28	242		192-242	8-47	8	1,000	1-10-61	6.00	6.1	5.5	.51	+72	+306	-30	14.7
22	AWW No. 2, across stream	De 2	15	250			1942	Flowing	2,000	1-10-61	5.94	6.1	6.6	.78	+48	+282	-202	14.7
24	AWW No. 5, near dam	De 46	26		248		7-47 / 5-20-61	12 / 25.1	1,000	1-10-61	6.02	6.0	6.5	.74	+8	+242	-40	14.5
25	AACSC, Pines, No. 2	CE 69	15	203	183	183-203	11- 6-59	10	450	11-30-60	5.31	5.5	12	1.2	-17	+216	-20	13.9
28	AWW No. 7, on hill (by filter plant)	De 88	120	347	287	287-345	11-24-61	113.75	600	1-10-61	6.14	6.4	8.7	.55	-45	+189	-30	14.7
30	Davidsonville Trans. New well	Dc 7	123	272	237	237-272	8-15-60	89.04	350		5.14	5.9	13	1.5	-48	+185	-32	13.8
32	U.S. Naval Acad., No. 9	Df 9	9	307		224-250 / 271-307	6- 6-61	1.05		11-30-60	6.20	5.8	14	4.1	-77	+158	-40	15.5
34	Crownsville State Hosp., No. 3, by dairy barn	Cd 43	130	285	252	252-285	9- 8-53	103	365	1-12-61	3.20	3.8	1.7	.39	-100	+123	-141	13.3
35	Sandy Point Prison Camp	Cg 8	19	272		257-272	1950	10		1-17-61	5.60		24	2.2	-121	+113	-103	14.5
36	Davidsonville Nike	Ed 24	130	310	300	300-310	11-54	148	60	1-19-61	6.87		6.0	1.8	-132	+103	-142	14.7
39	St. Margaret's Nike Control Area	Cf 38	85	271	260	260-270	1-18-55	52	20	1-18-61	6.11		23.0	2.6	-241	-7	-118	14.5
41	St. Margaret's Launching Area	Cf 39	30	283	270	270-283	1-28-55	17	28	1-18-61	6.20		26	2.9	-253	-20	-190	14.4
						Aquia Greensand												
14	Charter House Motel	Cf 79	100	128	123	123-128	4-21-59	63	30	1-11-61	5.50	5.6	0.40	0.04	+350	+582	+50	13.2
38	Lothian School	Fd 20	170	304	299	299-304	1956	162	25	1-12-61	7.42	7.6	.39	.04	-180	+55	-140	15.8
40	Holly Grove School	Ff 16	129	379		372-379	4- 6-51	170	65	1-16-61	7.79		.43	.05	-248	-13	-248	15.8

Eh AND pH CONTROLS ON IRON CONCENTRATION

The field and laboratory data are shown as a typical Eh-pH diagram in figure 8. The points are shown by symbols representing the aquifer and the analyzed total molality of the ferrous plus ferric ions indicated next to the points. A horizontal isopleth would indicate that the iron concentrations are independent of pH; a vertical isopleth indicates the reaction is Eh independent. The isopleths shown on figure 8 have slopes that demonstrate the pH and Eh control on the concentrations of iron in ground water. The values of the isopleths indicate the amount of iron as a function of Eh and pH that can be expected in water from this area. The greatest amount of iron (below isopleth $10^{-3.5}$) occurs where the pH is between about 5.0 and 6.5 and the Eh is less than about 200 mv. Note that in water with pH values less than 5, the iron concentrations are not the greatest, but rather have a wide range between $10^{-3.69}$ and $10^{-6.75}$.

The samples from each aquifer tend to cluster according to Eh, pH or iron content. For instance, the Patuxent samples have pH between 4.5 and 4.8 and iron content between $10^{-5.17}$ (0.38 ppm) and $10^{-4.74}$ (1.01 ppm). Most of the samples from the Patapsco Formation have pH between 4.0 and 5.1. The wide range in iron concentration was discussed in an earlier section as a function of the flow path and resulting oxidation potential. With the exception of two samples (18 and 34) the water from the Magothy and Raritan Formations has a pH greater than 4.9 and the iron content is more than about 10^{-4} (5.6 ppm). Although the pH of samples from the Aquia greensand ranges from 5.50 to 7.79, the iron content is nearly uniform, ranging from 0.43 to 0.48 ppm (about $10^{-5.1}$). The sample with the lowest pH, 5.50, has the highest oxidation potential, +582 mv, and the sample with highest pH, 7.79, has the lowest Eh, −13 mv; the third sample has an intermediate value for both variables. The equal iron content of all three samples may indicate that this water is in equilibrium with an iron-bearing mineral that was not studied during this investigation.

A rigorous geochemical interpretation of the field and laboratory data has been presented (Barnes and Back, 1964) and only the general procedure and conclusions are here summarized. Hem and Cropper (1959) concluded after an extensive study of iron in natural waters that the behavior of $Fe(OH)_3(c)$ (hematite) was the chief control on the solubility of iron. In the prediction of the distribution of ferric species the following reactions and equilibrium constants from Hem and Cropper were used:
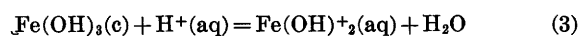
$$Fe(OH)_3(c) + 3H^+(aq) = Fe^{+3}(aq) + 3H_2O \tag{1}$$
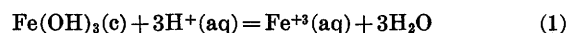
for which

$$K_1 = \frac{[Fe^{+3}][H_2O]^3}{[Fe(OH)_3][H^+]^3} = 6.9 \times 10^4$$

K_1 is the equilibrium constant for reaction (1).

$$Fe(OH)_3(c) + 2H^+(aq) = Fe(OH)^{+2}(aq) + 2H_2O \tag{2}$$
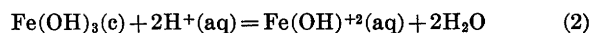
for which

$$K_2 = \frac{[Fe(OH)^{+2}][H_2O]^2}{[Fe(OH)_3][H^+]^2} = 2.6 \times 10^2$$

$$Fe(OH)_3(c) + H^+(aq) = Fe(OH)^+{}_2(aq) + H_2O \tag{3}$$

for which

$$K_3 = \frac{[Fe(OH)^+{}_2][H_2O]}{[Fe(OH)_3][H^+]} = 5.3 \times 10^{-3}$$
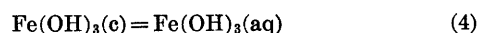
$$Fe(OH)_3(c) = Fe(OH)_3(aq) \tag{4}$$

$$K_4 = \frac{[Fe(OH)_3(aq)]}{[Fe(OH)_3(c)]} = 3.1 \times 10^{-9}$$

An integrated form of the van't Hoff equation,

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^\circ}{RT^2}$$

where H° is enthalpy, T is temperature in $^\circ K$ and R is the gas constant, was used to obtain the expressions for the temperature dependence of equilibrium constants as follows:

$$\log K_1 = -9.351 + 4.231 \times 10^3 T^{-1}$$

$$\log K_2 = -2.746 + 1.538 \times 10^3 T^{-1}$$

Enthalpy and entropy data are not available to determine the temperature variation of K_3 and K_4.

For water with no ferrous iron these four reactions were used to calculate the concentration of ferric species that would be present if water were in equilibrium with $Fe(OH)_3$. It is seen from table 6 that the analyzed and calculated values are of the same order of magnitude. Exact agreement is not expected because the concentrations of the ferric species are near the lower limit of detection.

TABLE 3.—*Concentration of total ferric species, in parts per million*

[Barnes and Back, 1964]

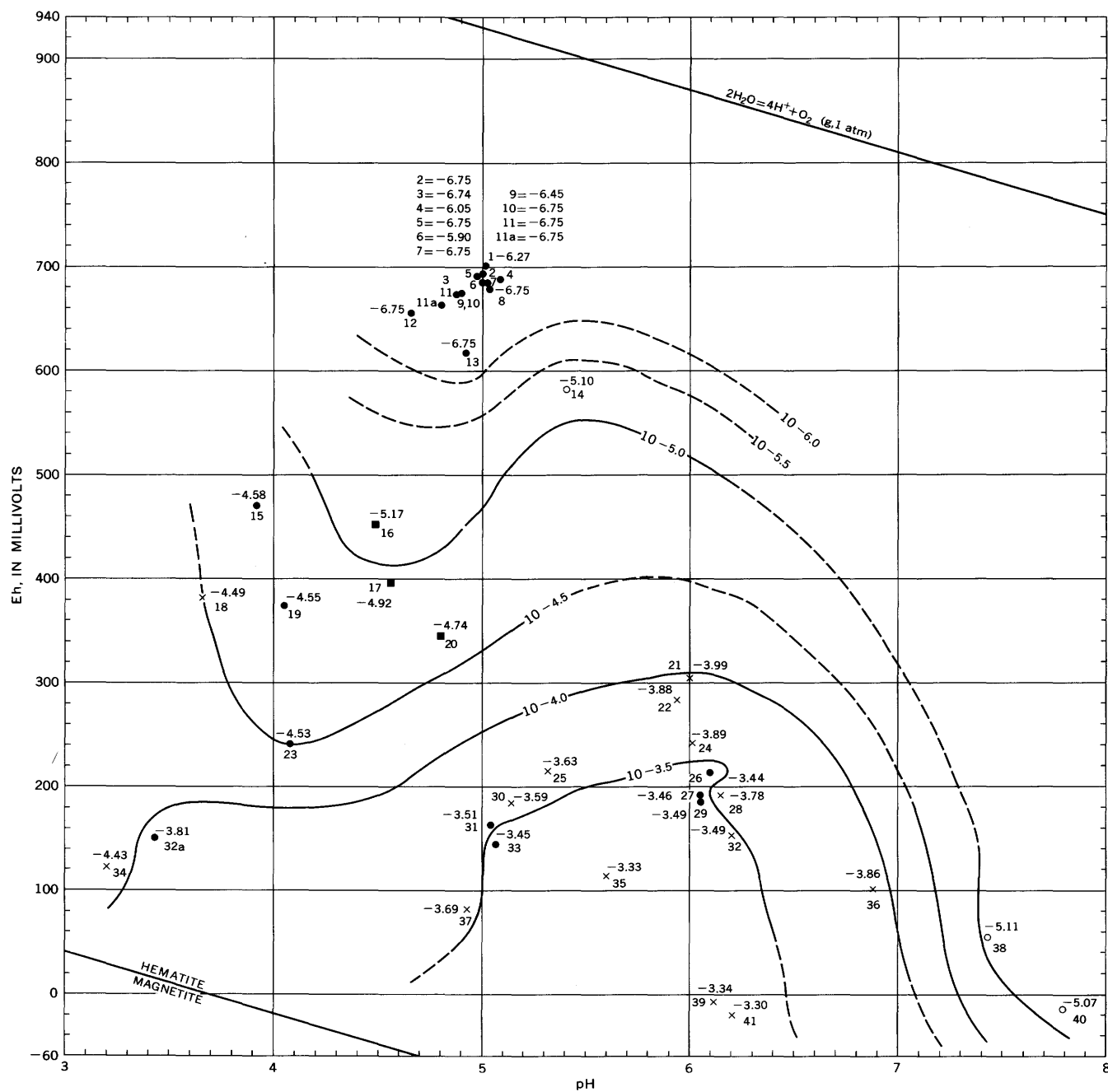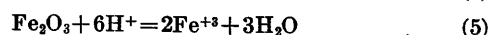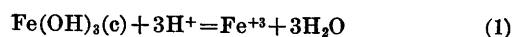| No. on fig. 3	Analyzed	Calculated at saturation
1	0.03	0.01
2	.01	.01
3	.01	.01
4	.05	.001
5	.01	.01
6	.02	.01
7	.00	.01
8	.01	.01
9	.02	.01
10	.00	.01
11	.01	.01
11A	.01	.01
12	.01	.01
13	.01	.01

FIGURE 8.—Eh-pH diagram from field observation showing isopleths for the total molality of the ferrous and ferric ions. Symbols: ⊙, Aquia; �

▪, Patuxent; ✕, Raritan-Magothy; ●, Patapsco.

From the distribution of ferric species (Barnes and Back, 1964, fig. 4) it may be concluded that at a pH greater than 5.05, the total concentration of ferric species would be below the limit of detection by the analytical methods used in this study. As a consequence, for any sample of pH 5.05 or greater, all the iron reported by analysis may be regarded as ferrous ion. In order to determine whether the theoretical models from electrochemistry explain the behavior of iron species under field conditions as observed during this study, reactions involving ferrous and ferric ions, and $Fe(OH)_3$ or hematite can be examined as follows:

$$Fe(OH)_3(c) + 3H^+ = Fe^{+3} + 3H_2O \qquad (1)$$

and
$$Fe_2O_3 + 6H^+ = 2Fe^{+3} + 3H_2O \qquad (5)$$

$$Fe^{+2} = Fe^{+3} + e^- \qquad (6)$$

The activities of the ferric ion were calculated using reactions 1 and 5. Equilibrium constants were corrected to the temperature of the water sample by use of the van't Hoff equation. The ferrous-ion activities were obtained by

$$[Fe^{+2}] = (Fe^{+2})\gamma Fe^{+2},$$

where the parenthesis-indicated molality was obtained from laboratory analysis and γ, the activity coefficient, was calculated from the Debye-Hückel equation at the temperature of the water.

The activities thus obtained were used with reaction 6 and the Nernst equation,

$$Eh = E^\circ + \frac{RT}{nF} \ln\left[\frac{Fe^{+3}}{Fe^{+2}}\right]$$

to calculate Eh values. Values for the standard potential, E°, at the temperature of the ground water were calculated from an integrated form of the Gibbs-Helmholtz equation.

$$d\left(\frac{E}{T}\right) = \frac{\Delta H^\circ}{nF} \, d\left(\frac{1}{T}\right)$$

The oxidation potentials measured in the field and calculated from both $Fe(OH)_3(c)$ and hematite are given in table 7.

The data indicate that the Eh data are usually more reliably predicted from the behavior of $Fe(OH)_3(c)$ but that in most cases the behavior of the mineral controlling the concentration of Fe^{+3} in the water lies between the properties of freshly precipitated $Fe(OH)_3$ (c) and hematite. This means that more iron is in solution than would be if hematite were the controlling phase, and less iron is in solution if $Fe(OH)_3(c)$ were the controlling phase. These results are consonant with the current view that the ferric oxhydroxide species in nature behave as varying states of dehydration of Fe $(OH)_3(c)$.

Table 4.—Measured and calculated values of Eh, in millivolts

[Barnes and Back, 1964]

Sample	Measured bright Pt electrode	Calculated from the data for $Fe(OH)_3(c)$	Calculated from the data for $Fe_2O_3(c)$
15	471	660	311
16	455	597	246
17	397	565	220
18	384	348	700
19	375	628	279
20	345	515	170
21	306	271	−80
22	282	274	−73
23	243	627	279
24	242	260	−87
25	216	370	20
26	214	217	−124
27	190	224	−120
28	189	232	−120
30	185	394	45
31	164	405	48
32	158	204	−142
32A	153	699	352
33	145	392	49
34	123	774	425
35	113	306	−41
36	103	107	−240
37	82	438	90
38	55	86	−259
39	−7	213	−134
41	−20	198	−151

CONCLUSIONS

Based on the foregoing analysis and interpretation of the field data it is concluded that the equipment, techniques, and procedures used are adequate for measuring valid oxidation potentials in ground water. The sampling must be continuous to provide an uncontaminated sample for oxidation potential measurements. The gold electrode was found to be less responsive and therefore presumably less reliable than the bright platinum electrode.

Contact with the atmosphere affects the oxidation potential of the water; oxygenated water tends to have a potential higher than natural water with no oxygen. Within the same aquifer the oxidation potential is higher in areas of recharge than it is in areas of discharge. The oxidation potential is one variable that controls the occurrence and concentration of iron in water. A relationship was found among the oxidation state and amount of iron in water, the ground-water flow pattern, and the mineralogy and organic content of the deposits. This statement probably is a valid generalization for any hydrologic system that contains iron-bearing sediments and oxidizable material.

The difference and changes in Eh within a hydrologic system can be used to substantiate conclusions based on other hydrologic data regarding source and movement

of ground water. For example, the Eh in the Patuxent Formation (350 to 450 mv) is about 300 mv lower than the Eh in the overlying Patapsco Formation (600 to 200 mv, pl. 1) in the Glen Burnie area. The Patapsco Formation has a wide range of oxidation potentials from about 145 to 700 mv; the highest potentials are in the recharge area. The oxidation potentials for water from the Magothy and Raritan Formations tend to be lower than those for the underlying formations, probably due to a greater amount of reduced material and decomposable organic matter in the Magothy and Raritan Formations. Inconclusive evidence suggests that oxidation potentials may show a seasonal variation in shallow aquifers; this would lead to seasonal variation in concentration of iron in water.

Interpretation of field-measured potentials of Eh and pH can enhance our understanding of occurrence of elements that exist in more than one valence state in water. Ranges of concentrations of iron in water can be predicted as a function of Eh and pH together. The Eh values measured in the field are between the values predicted from the solubility of $Fe(OH)_3(c)$ and the solubility of hematite. These results are consistent with the current view that the ferric oxyhydroxide species in nature behave as varying states of dehydration of $Fe(OH)_3(c)$. The upper limit of solubility of ferric ions may be predicted by using the solubility data for $Fe(OH)_3(c)$ and the lower limit is predictable from the solubility of hematite. In this study the concentration of $Fe^{+3}(aq)$ in oxygenated water is of the order of magnitude of that predicted from the $Fe(OH)_3(c)$ solubility. In low Eh waters, Eh values calculated by assuming hematite to be the control on the solubility of ferric species, were closer to the observed values than values based on the solubility of $Fe(OH)_3(c)$. The results of this study are in agreement with the postulate that low Eh conditions lead to selective leaching of more soluble ferric oxyhydroxide phases to leave hematite as the last ferric phase to dissolve.

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