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ACTIVATED CARBON USED AS ELECTRODES IN ELECTROCHEMICAL DEMINERALIZATION OF SALINE WATER

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ACTIVATED CARBON USED AS ELECTRODES IN ELECTROCHEMICAL DEMINERALIZATION OF SALINE WATER

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ACTIVATED CARBON USED AS ELECTRODES IN ELECTROCHEMICAL DEMINERALIZATION OF SALINE WATER

I. INTRODUCTION

For the past ten years a group at the University of Oklahoma under sponsorship of the Office of Saline Water, U.S. Department of Interior, and directed by Dr. George W. Murphy has been engaged in evaluation and research of electrochemical demineralization of saline water. Past members of this group have tested and evaluated methods and materials based upon porous carbons as electrodes for the electrochemical process. The choice of these materials for electrodes was based upon the high surface area and electrical conductivity combined with the inexpensive availability of commerical carbons.

The removal of ionic species from saline solutions by an electrochemical process is based upon the ability of the electrodes to take up and hold the ions in some form until conditions permit the desired release of the ions. Electrodes for such a process must therefore have the capacity to remove a considerable quantity of salt quickly, be physically stable under such conditions as are necessary for the salt removal, and be reversible in the ability to regenerate all of the salt under the proper conditions. It is also desired that the electrode materials be low in cost and easy to fabricate in the finished form, and that the conditions necessary for both salt demineralization and regeneration be simple and controllable with normal equipment and facilities. The electrodes should be responsive to either cations or anions, but not both, for efficiency of salt removal.

Electrodes and associated methods have been previously developed on this project which satisfy the above requirements for cation removal from saline solutions. These cation-responsive electrodes are constructed from powdered porous, commercial charcoal and graphite which are activated chemically to increase the capacity for cations and are prepared from aqueous slurries as a paste upon an inert porous backing material. The activated carbon electrode is incorporated with an anion-responsive electrode into a small, simple demineralization cell. The electrodes are maintained at a constant potential difference as saline solutions flow through the cell. Salt is thus removed by electrically induced ionic adsorption when the cation-responsive carbon electrode is made negative (i.e. cathodic) with respect to the other electrode (the anode); regeneration of the salt is then accomplished by simply reversing the polarity of the cell (i.e., the carbon electrode becomes positive).

Work in recent years has centered on the developed electrodes and their salt-removing ability with varied operating parameters. This was done for the purpose of obtaining basic knowledge about the cation capacity of the carbon electrode under various conditions, in order to develop the optimum materials and conditions for the electrochemical process. During the studies the lack of information about the activated carbon itself became apparent and work was undertaken to characterize the activated charcoal-graphite.

The present studies have been concerned with the determination of the carbon's macroscopic properties with the purpose of elucidating the microscopic structure of the carbon surface. Activated carbons have been shown to have organic functional groups covering the surface which have great influence upon the observed properties. Experiments have been conducted to determine the types and amounts of functional groups, and their relationship to the salt-removing capacity of the carbon when used as an electrode. Precision of the determinations has been limited by the reproducibility of preparation and activation of the charcoal-graphite.

All of the present work has been concerned with determining the properties of the chemically activated charcoal-graphite which has been used as the cation-responsive electrode in the demineralization cells developed and studied at the University of Oklahoma.

II. FUNCTIONALITY OF CARBONS

Physical Structure of Carbon

The term "carbon" as commonly used includes a multitude of materials which are composed mainly of elemental carbon. This classification covers the pure forms of the element, diamond and graphite, and the non-specific forms such as charcoals, carbon blacks, chars, and coal. Only graphite and diamond are true compounds with crystal structures and definite properties, while the rest are often referred to as being amorphous. Charcoals, blacks, and graphite are of major interest here and will be considered in some detail, but many of the properties discussed are common to all.

The elemental composition of graphite is not entirely pure carbon. Of course, natural graphite contains some of the minerals which are found in the locality, usually composed of silicates and oxides and referred to as "ash" in studies on graphite. But even an artifical graphite carefully made from a carbon-rich base will contain small amounts of sulfur, oxygen, and hydrogen. All three are residues from the environment or precursor and the oxygen and sulfur (as well as some of the hydrogen) can be considered to be contaminants either included interstitially or as substitutions at faults in the graphite lattice. More important, and always present even in a perfect crystal, are the hydrogen atoms which satisfy the valence requirements of the atoms located at the edges of the familiar aromatic sheets of carbon.

The analyses of blacks indicate that most have 91—99.8% carbon, 0.3—0.9% hydrogen, 0.0—0.7% sulfur, 0—3% oxygen, and 0.01—0.3% ash, by weight (1). The values for charcoals cover much broader ranges, with as much oxygen as 15—20% in some samples and the ash, depending on the source of the parental material, sometimes reaching 10—12%. The ash should be considered as a contaminant in all cases but is actually the source of observed properties for many measurements that have been made. The ash is usually SiO_2 and Fe_2O_3 with respectable amounts of Al_2O_3, S, CaO, MgO and traces of metals and other salts in natural graphites and various combinations of these in charcoals and blacks.

The lattice structure of graphite will be used as a base for discussion since blacks and charcoal resemble graphite to a limited degree on the microscopic scale. Finely divided graphite also constitutes one of the components of the carbon used in the present studies.

Graphite is comprised of very extensive parallel sheets of aromatic six-membered rings. The sheets consist of covalently bonded carbon atoms with C—C distances of 1.415 A and some of the properties of large aromatic organic molecules, i.e. high electrical conductivity across the sheet. The sheets are only weakly held to each other at a distance of 3.354 A by dispersion forces (van der Waal's) as a result of orientation. Atoms in one sheet are not directly above atoms in the sheet below but are displaced a distance sufficient for the atom to be centered over the hexagon ring of the other sheet, as shown in Figure 1. This results in every other layer being identical in position, thus an ABABA... arrangement. Another possible arrangement, resulting in a rhombohedral lattice, is represented by ABCABCA... where a sheet is in identical positions with

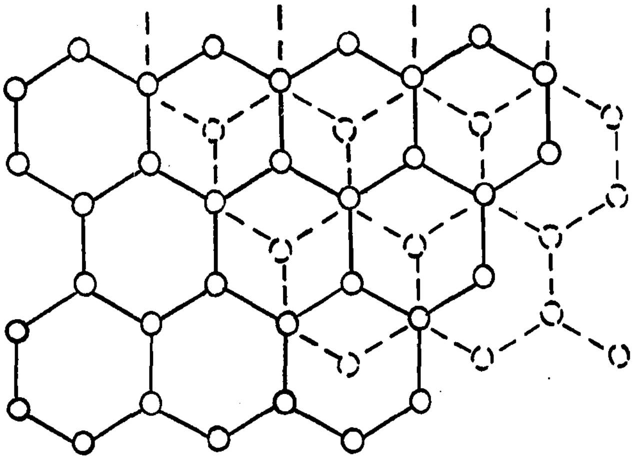


Figure 1. The Graphite Lattice. Sheets of hexagon rings of carbon atoms, where the sheet directly below is represented by the dashed rings.

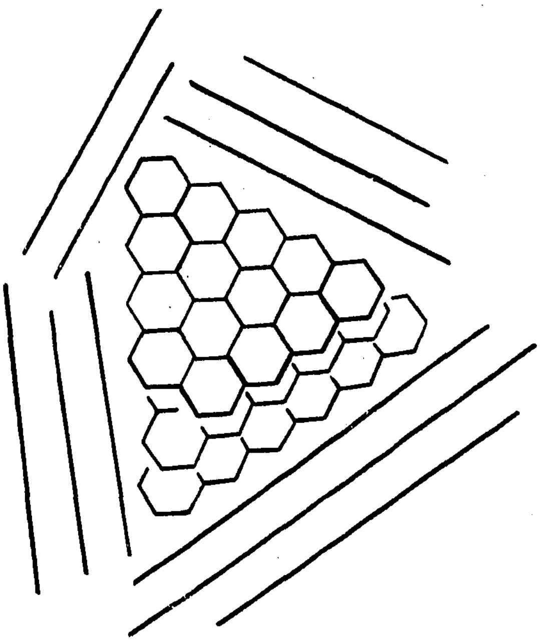


Figure 2. Representation of Amorphous Carbon Particle. The particle consists of randomly oriented graphite-like aromatic sheets. Some are seen on edge while others have the basal plane exposed.

the third one above and below it. Close examination of x-ray analyses on natural graphites have found distributions for the layered sheets such as: 80% in the normal hexagonal (ABAB) form, 14% in the rhombohedral (ABCABC) form, and 6% disordered (referred to as "turbostratic") (2, 3).

The latter orientation (actually lack of orientation) is the major way in which carbon is found in blacks. Small aromatic plates with widths of 10—30A condense out from the carbon black process. The sheets are usually in stacks of 3—5 layers, but not oriented to each other in any sort of organization. Some remnants of the aliphatic precursor can still be found and smaller aliphatic groups are formed, no doubt linking or situated on the aromatic sheets as well as being interspersed in a random fashion among the crystallites. The carbon in blacks is found to be 60—90% in parallel layers, 4—26% as random, and up to 30% in single sheets. The 10—30A thick platelets composed of the parallel layers are considered to be crystallites, i.e. having some degree of regular ordering, basically similar to graphite (1, 4). A representation of carbon black is shown in Figure 2. The average interplanar distance for blacks is 3.5A, compared to 3.35A for graphite, i.e. the planes do not stack together so tightly when there is a lack of orientation.

Charcoals also contain crystallites, but not nearly as many as blacks because they retain some of the carbon skeleton of the source material, whether it is wood, nut shells, etc. Being from natural products charcoals have a much more varied structure than any other carbon material and this is shown by their porous nature and large surface areas. Some blacks also have large surface areas but this is due to their extremely small particle size, usually just a few hundred A in diameter, for they lack the porosity of charcoals. Carbon black particles are small enough that a black appears light and fluffy and has a low average density.

With the high porosity of charcoals the density is lower than that for graphite and the total volume of the pores sometimes is above one cubic centimeter per gram of charcoal. The majority of the pores are in the micropore range (radii = 8—20A) with volumes of 0.2—0.6 cm^3/g and the high surface area is due mostly to the micropores instead of particle size or the larger macropores (radii = 1000A up) and transitional pores (with radii between the other two). The micropore structure is probably due to faulty and disordered arrangements of atoms which are destroyed by the activation process (5, 6, 7).

The carbonization of organic materials by heating to 200^{o}-500^{o}C with little air results in chars and charcoals. Blacks are formed by essentially the same process using hydrocarbon gases and oils at other temperatures in a flowing method, often collecting, and thus controlling, the products on cold surfaces. Heating almost any carbon material, in little or no oxygen to 3000^{o}C causes graphitization, the process of becoming graphite-like. Graphitization starts at 1700^{o}-2000^{o}C, depending upon the gases present, and is a well-established process by 2500^{o}-2700^{o}C. Extensive aromatic sheets are formed, the density increases, pores and random groups are destroyed, with other properties approaching that of graphite, e.g. the conductivity increases (6, 7).

The lower and intermediate temperature ranges of 25^{o}-1200^{o}C are quite susceptible to reaction with many gases and solutions. Controlling the reactions, usually some form of oxidation, to alter but not destroy the carbon is referred to as activation.

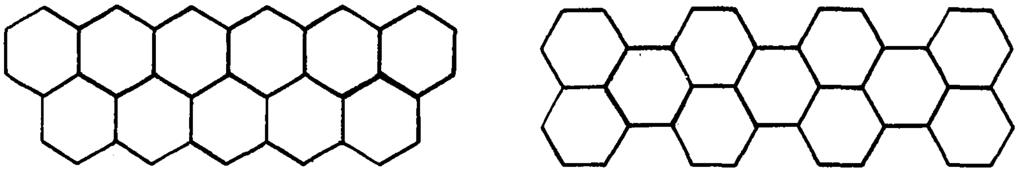
Surface Functional Groups from Activation

The alteration of a material by physical or chemical treatment is called activation or passivation--the increasing or decreasing of desired properties. Carbons are activated usually by an oxidizing medium and made passive by heating to high temperatures with little or no oxidizers present to establish more and larger crystallites by graphitization.

Commonly, activation of carbons is by O_2, air, NO_2, CO_2, HNO_3, $NaOCl_4$, O_3, and HNO_3-H_2SO_4, as well as many others which have been used, including the mild agent H_2O. The process of activation involves attack on exposed carbon atoms, usually those located as aliphatic chains or groups, end and edge carbons on the aromatic sheets, and in general, those described previously as random and disordered. In other words, the oxidizer reacts with almost any carbon atom not located within the strong covalently bonded sheets found in crystallites and crystals. (Attack has been found on the basal planes of graphite with such reagents as atomic oxygen (8).) The edges of single crystals of graphite were found to be twenty times more reactive to oxygen at 800°C than the basal planes, even upon repeated exposure of fresh faces by cleavage.

Activation with strong oxidizers yields gaseous oxides of the carbon and reagent as by products during the process, often with the generation of heat, e.g. in the mixed-acid treatment with HNO_3-H_2SO_4, dark brown clouds of NO_2 and N_2O_3 are given off as well as CO_2, CO, and H_2O with obvious vigorous action and the generation of much heat (9). Even activation with H_2O at elevated temperatures yields H_2 and CO_2. The carbon given off as CO and CO_2 during activation is no doubt mostly composed of that previously located as small aliphatic groups and random chains in blacks and charcoals. This type of burn-off can result in high weight loss of carbon. Thus much of the random carbon is destroyed in burn-off with the subsequent creation of pores and spaces. This is the source of the characteristic high porosity found in activated charcoals.

The attack yields a more important product, the imparting of oxygen to the carbon surface with strong bonds, i.e. chemisorption of oxygen. This attachment of oxygen to the carbon matrix occurs at active sites which are associated with centers of unpaired electrons, or free radicals (7, 10, 11). The chemisorption of oxygen markedly reduces electron spin resonance of the carbons (12). Walker *et al.* have demonstrated that there are at least two and possibly three such types of active sites by dry oxygen chemisorption on the edges of a highly graphitized black (13). Faults and impurities in graphite crystals also act as initial points of attack and result in etching of hexagonal patterns which can be detected by electron microscopy. The edges of graphite sheets prefer a zigzag structure as opposed to an arm chair arrangement (8, 14) and it is assumed that this is the prevalent form of the crystallites after activation.



Zigzag Form

Arm Chair Form

Figure 3. The Edges of Graphite Sheets, from G. R. Hennig.

Processing and preparation imparts some oxygen to carbons by grinding, etc. in air, but this is often a low amount, only 0.5—1.0% in blacks; while an activated charcoal contains from 5—20% oxygen by weight and the most highly oxidized form of a carbon, graphitic oxide, contains 37—40% oxygen (15). Other elements are present too, especially hydrogen, and minor amounts of sulfur and nitrogen, which are the result of the activation method or ash content, but oxides are the most abundant form of surface groups. Oxygen is also associated with the activated carbons in the form of physically adsorbed H_2O and O_2, with erroneous results often obtained in studies because of later reaction of these species with the surface oxides and the carbon itself.

A freshly exposed surface, by thermal outgassing or physical means, is quite reactive. The heat of chemisorption is quite high for the first molecular attacks and drops in value as the surface is covered more and more with oxides; thus it appears that the oxides play a role in the further oxidation-activation of carbons. This same type of effect is seen also in degassing and graphitization. The presence of small amounts of O_2, CO_2, or H_2O aids in forming the graphite sheets at lower possible temperatures in graphitization, perhaps as the result of momentary formation of an oxide to satisfy an unfilled valence.

Even oxidation end products such as CO_2 and H_2O form oxides under the proper conditions. Carbon dioxide reacts with the carbon surface at temperatures as low as 450°C (16) in a reaction of the form:

$$CO_{2\,(g)} + C_{\substack{\text{active}\\\text{site}}} \rightleftarrows CO_{(g)} + C(O)_{\substack{\text{surface}\\\text{oxide}}} \qquad (1)$$

At 750°-850°C the rate of exchange of oxygen atoms between the gases and the surface is 10^4 times faster than the gasification of the carbon atoms as additional CO or CO_2, as determined with carbon 14. The reaction proceeds up to 1000°C where the surface oxide is no longer stable and the rate of gasification of carbon overcomes the rate of oxygen exchange (17, 18, 19, 20).

Identification of Surface Oxides

The groups formed on the carbon particle surface from activation have organic functionality. They react with alcohols, bases, diazomethane, thionyl chloride, *p*-nitrobenzoyl chloride, Grignard reagents, and give responses to measurements with IR, polarographic techniques, adsorption, and some magnetic and electron spin techniques. By means of these tests and methods many forms of the oxides have been postulated and identified. The results are not entirely without question because of the presence of the large carbon matrix, which tends to cloud or obscure measurements. A carbon usually has many types of groups and the close proximity of other groups to one often changes its form so that they together behave as a new third type. The presence of water, temperature of measurement, and in general the conditions of activation, storage, and evaluation have effects upon the form of the oxides. In addition, wet strong oxidizers impart almost all forms of oxides ever identified to a carbon sample. Thus the measurements upon such a substance are lacking in the normally accepted precision because the activated carbons themselves do not have reproducible forms or amounts of surface oxides within that precision.

Earlier work on activation of charcoal and the resulting effects upon observed properties was reviewed by Steenberg in 1944 (21), after many investigations over the years with conflicting results and conclusions. A flourish of work was begun in the late 40's and early 50's resulting in the biennial conferences on carbon begun at Buffalo in 1953. But the most effective work has been done since that date with interpretations from many sources arriving at the same general conclusions about surface groups, even though the actual samples vary greatly. (The publications on the subject of carbon have reached tremendous proportions in the last ten years.) H. P. Boehm *et al.* (22, 23) at the University of Heidelberg have identified the oxides on sugar charcoals and other carbons as consisting of four groups, the distribution and alteration of which are functions of whether the activation is by gas at 400°C or by oxidizing solutions at room temperatures. These groups are carboxyl, phenolic hydroxyl, carbonyl, and a lactone-lactol resulting from interaction by hydrogen bonding of carboxyl and carbonyl, as shown in Figure 4. The distribution was found to be equal amounts of each of the four with activation by O_2 at 400°C, and two portions of free carboxyls to one of each of the others when activated with solutions of NaOCl, $KMnO_4$, or $(NH_4)_2S_2O_8$. This was determined by selective titrations of the acidic groups with increasing strength bases. It was reasoned from the results of titrations with $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$ that the weakest base (bicarbonate) neutralized the strongest acidic group (carboxyl), the next stronger base (carbonate) neutralized that same amount due to carboxyl plus the next stronger acid group (lactone), etc. and that the ethoxide neutralized all of the acidic groups as well as forming salts of

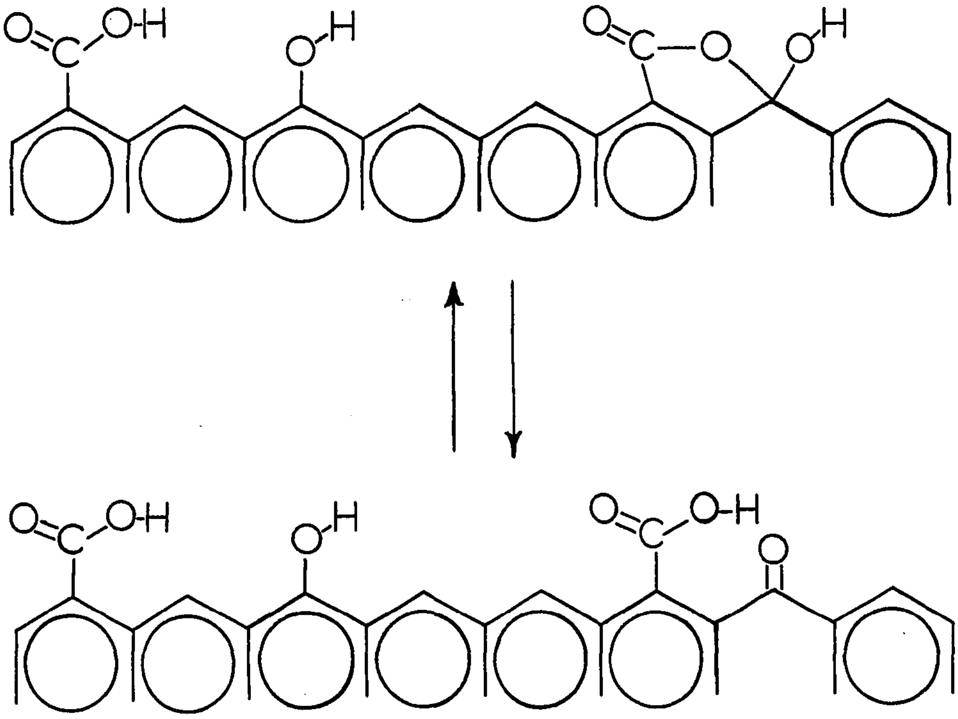


Figure 4. Surface Oxides Proposed by H. P. Boehm *et al.* The groups found on carbon include, left to right: carboxyl, phenolic hydroxyl, carboxyl that occurs as lactone-lactol, and carbonyl, which is often involved with the carboxyl to form the lactone-lactol.

hemiacetals with the carbonyls. The distributions and identifications were checked with other chemical methods, such as diazomethane for carboxyl. Treatment of the charcoals first with CO_2 at 950°C to expose more sites, then outgassing to 1100°C in nitrogen before oxidizing at 400°-450°C with O_2 increased the oxygen content and total number of groups to approximately 1.4 meq/g, more than that with just oxidation at 400°C by O_2. The wet oxidations yielded more oxides, mostly carboxyl groups, especially in the case of $(NH_4)_2S_2O_8$ which gave total acidity of 3.4 meq/g.

Smith, Young, and Smith (24) identified carbonyl groups from activation at room temperature with O_3 and O_2 by the infrared spectra of a thin carbon film. The activation with NO, O_2, and H_2O_2 at room temperature, N_2O at 400°-500°C, and H_2O at 100°C gave rise to lactone groups. All of the latter reacted quicker and to a greater extent at 400°-500°C. Phenolic hydroxyl groups were identified with H_2O and H_2O_2 activation at 100°C and higher temperatures.

Kiselev, Lygin, *et al.* (9, 11, 25) oxidized a black with NaOCl solutions and found carbonyl and hydroxyl, often hydrogen bonded together, identified from IR spectra. Carboxyls were also found for the above method of activation. Mixed-acid treatment with HNO_3-H_2SO_4 gave rise to all three groups to a level of 1.25 meq/g.

Nitric acid has been used by Donnet *et al.* (26, 27, 28) on blacks and they identified carboxyl, hydroxyl, and carbonyl groups by IR and various organic tests and eliminations.

Graphitic oxide is a special carbon that has been prepared from graphite by the action of $KClO_3$ in the presence of HNO_3-H_2SO_4 with the oxidation being so complete as to form almost a definite compound. Hydroxyl groups are found in abundance with some minor variation. The carbon atoms, which are only 50—57% of the total weight, are distributed as follows: 32.5% as C=C, 21.5% as COH, and 46.0% as linked to oxygen bridges (ether-aroxy) with an additional small amount (1.5—3.0%) found as carboxyl groups (15).

Other groups on carbons have also been postulated and identified, including ether, epoxy and aldehyde. The majority of the groups are carboxyl, carbonyl, and hydroxyl with variations and combinations of these to form lactones, aldehydes, carboxylates, anhydrides, etc. (29, 30, 31, 12, 6, 7).

In the present investigations the activated carbon which has been studied is a mixture of a commercial charcoal and finely divided graphite. The powdered Norit A charcoal (N), two parts by weight, is mixed with one part by weight of Dixon's Air-Spun 200-10 graphite (G) and activated with two volumes of sulfuric acid previously mixed with one volume of concentrated nitric acid (MA). The reaction is vigorous and the degree of oxidation is high. The activated carbon will be referred to throughout the rest of this paper as N:G (2:1) MA.

Evaluation of the Surface Oxides of N:G (2:1) MA

Titrations with Base

Finely divided activated carbons behave both as ion-exchangers and as sites for redox reactions. The latter function can be studied when the carbon is made into an electrode and a suitable potential is applied as discussed in a later section. Ion-exchange reactions can be, and have been, studied independently of the redox nature of the carbon when chemical potentials are used as the driving forces.

The ion-exchange properties are attributed to the acid-base nature of the carbons, i.e. the surface oxides. The surface oxides on carbons have been identified as carbonyl, carboxyl, phenolic hydroxyl and a possible combination of these to give a lactone-lactol group as well as others of minor importance. The relative amounts of these groups depends upon the method of activation, with solution oxidation at room temperature causing relatively more carboxyls to be formed. The numbers of these groups are large enough to permit titration like ordinary acids with reasonable amounts of carbon (21, 22, 32, 9, 33, 34).

Titrations have been done on the Norit:Graphite (2:1) Mixed-Acid treated carbon to determine the amounts and distribution of the acidic oxides. After some difficulty with obtaining reproducible results (because of unknown water content and equilibration time) a procedure was established to evaluate the acidity of N:G (2:1) MA.

Because of the porous nature of the carbons, they were not titrated in the usual sense of the word. Each measured point represents an individual sample of carbon which has been in contact with the basic solution for a specified time. At the end of this period portions of the supernatant solution above the now settled carbon were removed and titrated. Thus the adsorbed or reacted amount of base was determined by difference.

Previous to the titrations the carbon was placed in a 100% humidity chamber at 25.0°C for several days so that equilibration of adsorbed water would be established before introduction of the samples to the aqueous solutions. (More details on water content are to be found in a later section.) Extra portions were also withdrawn at the same time to determine the "per cent solids" of the samples.

The base was introduced to the weighed wet carbon samples and the containers sealed. The flasks were shaken intermittently and then the carbon was allowed to settle after sufficient time had passed for the acid-base reaction to reach equilibrium. Samples reached a constant level of ion uptake, within the limit of experimental error, by 24 hours for the higher concentrations, but all samples were allowed to stand 5-10 days in order to assure equilibrium. Two to four aliquots were withdrawn form the clear supernatant and titrated with standard HCl solutions.

The titrations of N:G (2:1) MA with NaOH, Na_2CO_3, and $NaHCO_3$ are presented in Figure 5. The samples were usually 2-3 g with 25—40% adsorbed H_2O and 25—50 ml of solution. Although the time of reactions were 5-10 days, it is likely that some small fraction of the reactions were still occurring even after than time. The concentrations used were not sufficient to establish the absolute limits of each group type but approached the final values, with the differences in group types well indicated.

The Na_2CO_3 and $NaHCO_3$ titrations were identical, but this was not always found to be reproducible. A few of the earlier $NaHCO_3$ titrations were found to neutralize lesser amounts than Na_2CO_3. The difference in those amounts (carbonate minus bicarbonate) was usually 0.2—0.3 meq/g. This small, non-precise difference could be an indication of the lactone present, i.e. that amount of carboxyl which in combination with adjacent carbonyls behaves as a weaker acid. The non-reproducibility of the

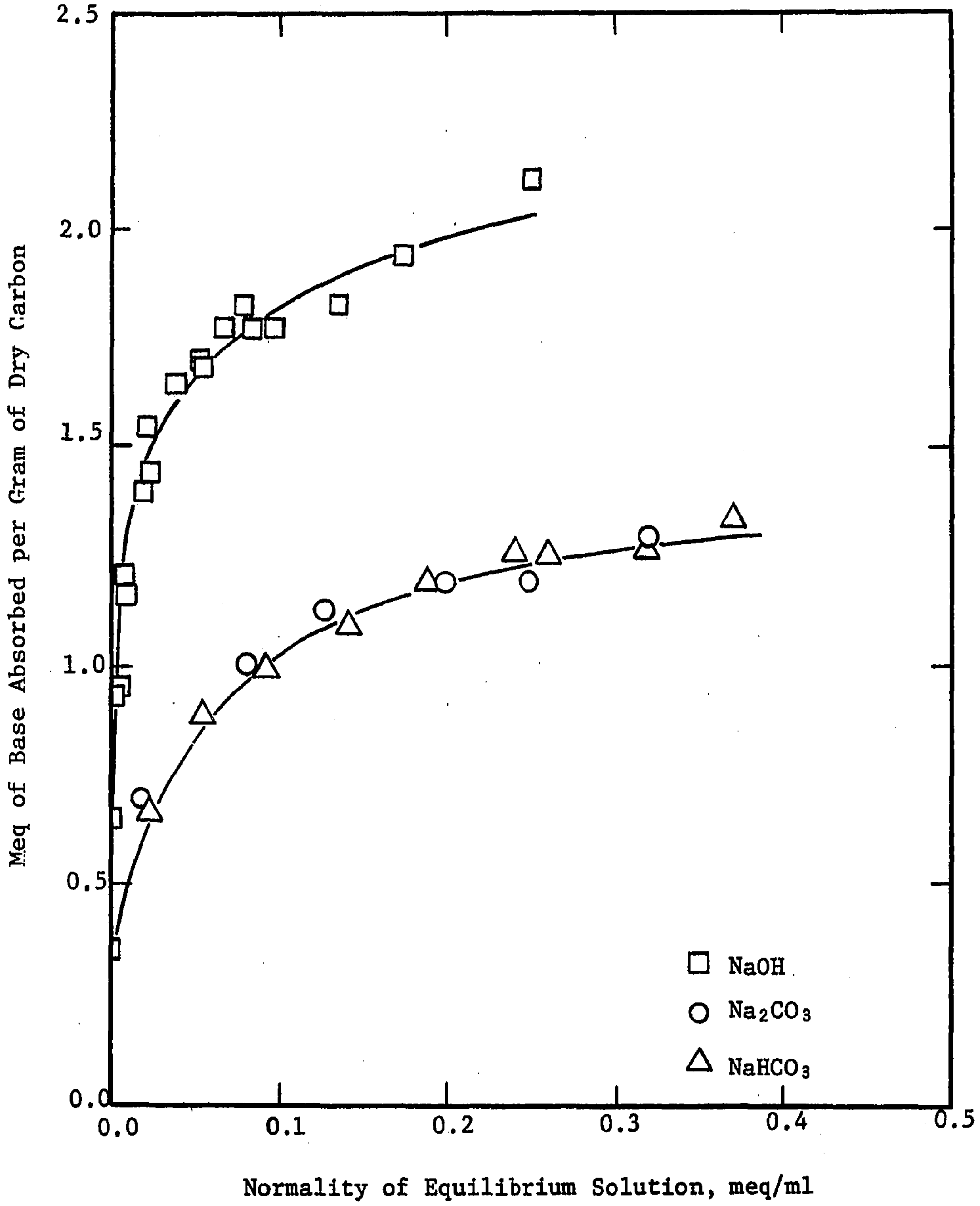


Figure 5. Titration of Norit:Graphite (2:1) Mixed-Acid Treated with Various Bases.

carbonate-bicarbonate difference may be the result of CO_2 from the atmosphere. Although the solutions were kept free of excess CO_2, the water vapor used in equilibration with the carbon was not.

The titrations show at least two distinct levels of acidity. The lower is due to the neutralization of carboxyl groups (22), and the difference between the hydroxide and carbonate-bicarbonate curves indicates the amount of phenolic hydroxyl groups present.

Carboxyls are in greater abundance, usually 50—65% of the total acidic groups. The hydroxyl groups on the carbon are nearly constant, being 0.75—0.77 meq/g over most of the entire concentration range.

It should be pointed out that some of the earlier literature values of NaOH adsorption are misleading in that the amount of base neutralized was determined with low concentration solutions and it is obvious from Figure 5 that the concentration of hydroxide must be high (and the times long) before the total acidity can be determined.

In trying to elucidate the amounts of other oxides the method of H. P. Boehm was followed and the N:G (2:1) MA was titrated with sodium ethoxide. This strong base should neutralize all acidic groups and form salts of hemiacetals with carbonyls; thus a difference between ethoxide and hydroxide curves would indicate the amount of carbonyl groups on the carbon.

Preparatory to titration with ethoxide, the carbon was first allowed to equilibrate with water vapor at 25°C. After drying at 110°-115°C for 3-4 weeks, individual samples of carbon were placed in an ethanol atmosphere at ambient temperatures. The alcohol had been dried with Mg and I_2 and the alcohol chambers were kept in a dry box to lessen the chance of water contamination when the carbon samples were removed for their daily weighings. The samples were kept in the ethanol vapor for five weeks. At the time of removal the carbon samples had adsorbed 6.7-7.1 meq ethanol per gram of dry carbon at 24^{o}-25^{o}C.

The sodium ethoxide-ethanol solutions were kept dry and introduced to the flasks, which were then sealed. The sodium ethoxide was prepared *in situ* from clean, dry sodium and the dry prepared alcohol. The samples were shaken randomly and allowed to equilibrate for 8-10 days. After the flasks were opened aliquots were removed and titrated with aqueous solutions.

In Figure 6 the ethoxide titrations are compared with the previous hydroxide curve. There is essentially no difference between the two bases except at low concentrations, where it reaches 0.4 meq/g. Actually there is a small difference at higher concentrations, but this is of the same size as the errors in the determinations, so that it cannot be stated definitely how many, if any, carbonyl groups are present. If they are present, it is only to a small degree. Carbonyls could be formed with the original activation and later be converted to hydroxyls with time and the presence of water, which is nearly always present in N:G (2:1) MA.

The titrations indicate that there is an abundance of carboxyl and hydroxyl with very little amounts of other groups present.

IR Spectra of Sodium Salts of N:G (2:1) MA

In trying to identify the surface oxides that had been characterized by the base titrations, attempts were made to run an infrared spectra with Nujol mulls and KBr pellets on the activated carbon. Even the tiniest amount of the carbon was too much for the latter method and the pellets

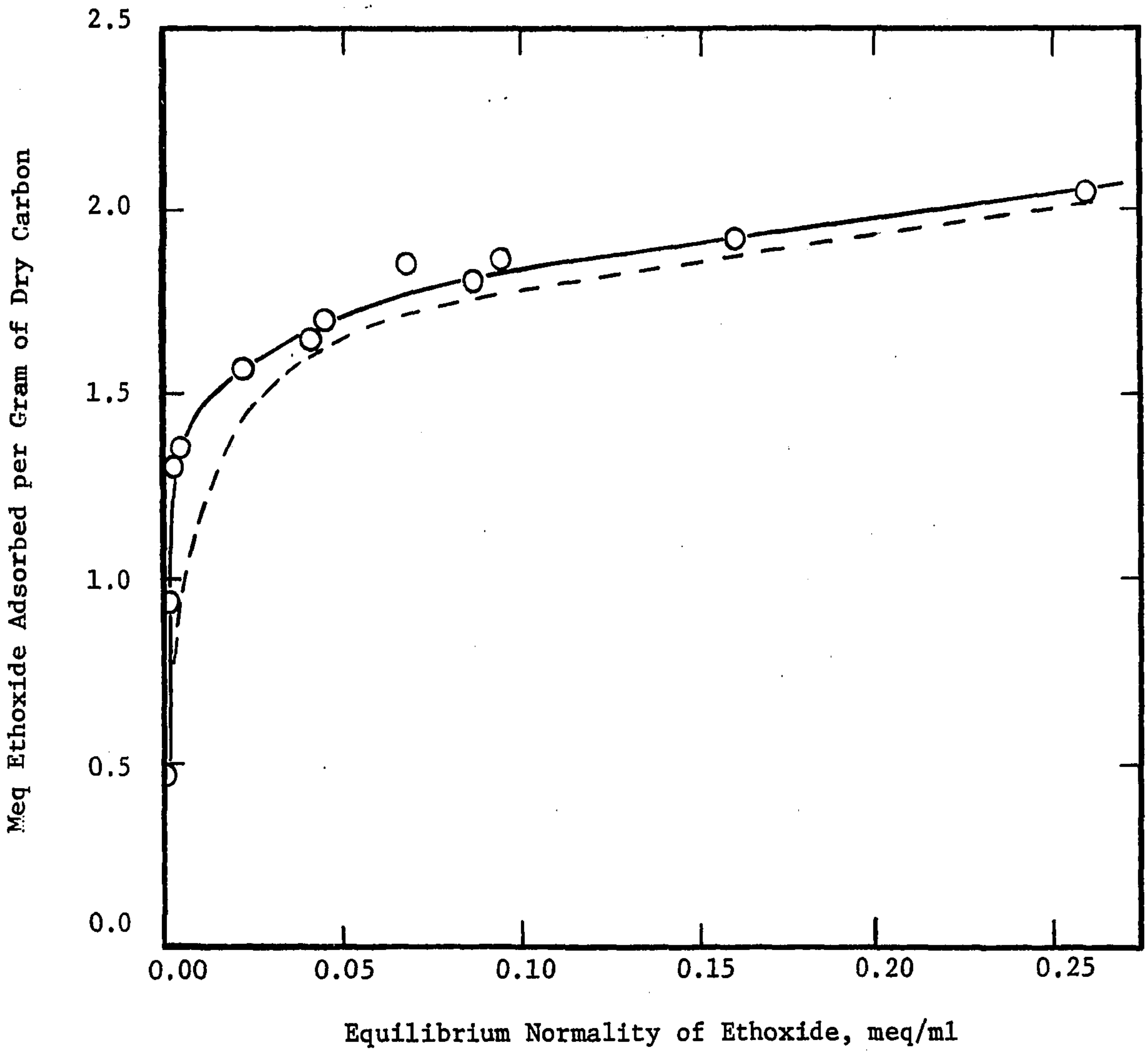


Figure 6. The Reaction of Sodium Ethoxide with N:G (2:1) MA. The carbon had been previously equilibrated with ethanol vapor at 25°C. The points and solid line are from two sets of data, and the dashed line is the smoothed results of identical titrations with aqueous sodium hydroxide.

had the appearance (and transmittance) of a very black, shiny button. With the high content of oxides and relatively low exposure of aromatic character (see Adsorption section) none of the carbon would go into the Nujol. Attempts were also made to obtain an IR reflectance spectra with a MgO mirror attachment, but again the results were the same--none!

For quite some time it had been noticed that the supernatant above the carbon samples in the base titrations was clear but yellow. The intensity varied with the pH, becoming dark yellow orange with high pH. Since the carbon is so finely ground and severely oxidized it was thought that the color was due to the suspension of very fine particles of the carbon held up by some form of colloidal action. It was decided to try for an infrared spectrum on this part of the carbon.

The supernatant liquids were withdrawn and evaporated to dryness at 110°C. The crystals were indeed yellow instead of the white of NaOH and Na_2CO_3, of which the evaporite was mainly composed. These were then made into KBr pellets for the IR analysis. It should be pointed out that not only are most carbons, such as the N:G (2:1) MA, black to the eye (the visible range) but because of their varied internal structure they are black to most of the IR range, too (due to both scattering and continuous absorption). The peaks that did show up were small blips on the much larger absorption of the Na_2CO_3, NaOH, and the carbon itself. Distinct peaks were obtained only when the KBr pellet was loaded with enough sample to cut transmission to the 20—60% level, and this was an extremely small amount.

The wave numbers and relative description of the resulting absorbances from scans on a Beckman IR-8 with KBr pellets are presented in Table I.

Table I

Infrared Spectra of Evaporated Suspensions of N:G (2:1) MA After Neutralization with Base

Frequencies (cm^{-1})	Na_2CO_3 Solutions		NaOH Solutions		
	#35	#42	#32	#33	#38
1070	w	w	—	—	—
1150	w	m	—	—	—
1155	—	—	m	m	m
1265	vw	m	m	m	m
1380	—	sh	sh	sh	sh
1560 (?)	—	—	vw	m	vw
1590	—	m	vw	m	w
1630 (?)	—	—	vw	w	w
1775	sh	sh	m	m	m
2480	*sh	*m	**m	**m	**vw
2850	sh	vw	—	vw	vw
2950	w	vw	—	—	—
3430	s	—	—	—	b
3440	—	s	—	b	—

s = strong
w = weak
m = medium
sh = sharp
vw = very weak
b = broad

* This band appears to be a doublet with a shoulder @ 2490 cm^{-1}.
** Appears as a doublet with shoulder @ 2500 cm^{-1}.

The 1150 band has shifted to 1155 cm^{-1} for the hydroxide samples. The 1560 and 1630 cm^{-1} bands are questionable and the 3430—3440 is broad.

These are not the peaks due to the original functional groups on the activated carbon, but rather those of the "sodium salt" of the carbon. The acids were neutralized, perhaps not to completion in all cases, and sodium ions were thus associated with the acidic groups.

The bands at 1590 and 1380 cm^{-1} are due to the carboxylate ion, which would normally be found as a carboxyl if it were not for the presence of sodium from the neutralization with base.

The band at 1775 cm^{-1} can be identified with a carbonyl but it is questionable as to which carbonyl. The literature points to a carbonyl of a lactone structure at this wavelength but since the lactone would open, at least partially, with high pH the peak could be due to the free carbonyl of cyclic ketones. That neutralized with Na_2CO_3 has a better defined band than that neutralized with the stronger NaOH, so 1775 cm^{-1} may be due to a lactone-type structure which was only partially neutralized.

The band at 1070 cm^{-1} is perhaps the C—O of a hydroxyl group, and it is noticed here only in the partially neutralized form, i.e. with Na_2CO_3 but not NaOH. The 1150—1155 cm^{-1} peak is associated with the stretching of this same group. The 1265 and 3440—3430 cm^{-1} bands might be due to the COH of the hydroxyl but there should be little of this left in the H form after NaOH neutralization. Possibly the 1265 and 1070 cm^{-1} bands could be due to an ether--an aryl ether.

The carboxylate ion has been reported for other oxidized carbons neutralized with NaOH. Garten *et al.* (29) reported a shift to 1590 from 1600 cm^{-1} for the sodium salt of Carbolac 1 and a similar shift from 1625 to 1610 cm^{-1} for the sodium salt of a sugar charcoal activated at 400°C. Kiselev *et al.* (11) noted bands at 1630 and 1410 cm^{-1} for their mixed-acid treated carbon black, and both shifted, to 1600 and 1460 cm^{-1}, respectively, with NaOH neutralization. They also report the disappearance of the 1730 cm^{-1} peak (carbonyl) with neutralization. Harker (12) states that NaOH neutralization of a highly acidic cellulose carbon shifted the 1582 peak to 1575, decreased the 1684 (carbonyl) to near oblivion, and caused the appearance of the 1370 cm^{-1} band. A black, oxidized with sodium hypochlorite, also showed a 1585 cm^{-1} peak (25). Thus, the presence of carboxyl-carboxylate on N:G (2:1) MA is confirmed for the proposals based upon the titrations.

Absorption for lactones and free carbonyls have been placed from 1560 to 1775 cm^{-1} on carbon. Most consider the carbonyl from a lactone to be in the range 1680—1760 cm^{-1} and state that it is diminished greatly or disappears altogether upon neutralization with NaOH. The free carbonyl has been placed at 1720—1760 cm^{-1} (29, 11, 12, 25, 24). For other systems carbonyls of lactones are reported from 1700—1800 cm^{-1} (35). The 1775 cm^{-1} peak appears to be a carbonyl, but the form of the carbonyl is not obvious from this work; it might even be associated with unionized carboxyl but this is unlikely.

The hydroxyl group, or sodium salt of the hydroxyl group, is shown with the 1070, 1150, 1265, and 3440—3430 cm^{-1} bands (25, 31). The latter has been identified in graphitic oxide (30, 15) and blacks oxidized with nitric acid (26).

Donnet *et al.* (26) attribute the 2850 and 2925 cm^{-1} bands to CH and CH_2 of aromatics so that the 2850 and 2950 cm^{-1} bands of the N:G (2:1) MA could be of the carbon itself. These two, and 2480 cm^{-1}, might be implications of hydrogen bonding, instead (35). There is not sufficient evidence to make a decision. Other investigations on the infrared spectra of carbons lead to inconclusive or questionable results (36, 37, 38, 39).

Thermal Decomposition of Surface Oxides

The surface oxides on carbon can be removed thermally, or "outgassed", by heating the activated carbons in an inert atmosphere or vacuum to 1000°-1200°C (40, 41, 42). This process involves the destruction of the outer edges of the carbon matrix and results in CO_2, CO, CH_4 as well as the expected H_2 and H_2O. Each gas is characteristic of a particular group if the gas is not a reaction product of the original gas and carbon or other gases. The production of these gases is thus the reverse of chemisorption, except that the products are not in their original form and they contain part of the parental carbon (43, 44, 45, 46, 47).

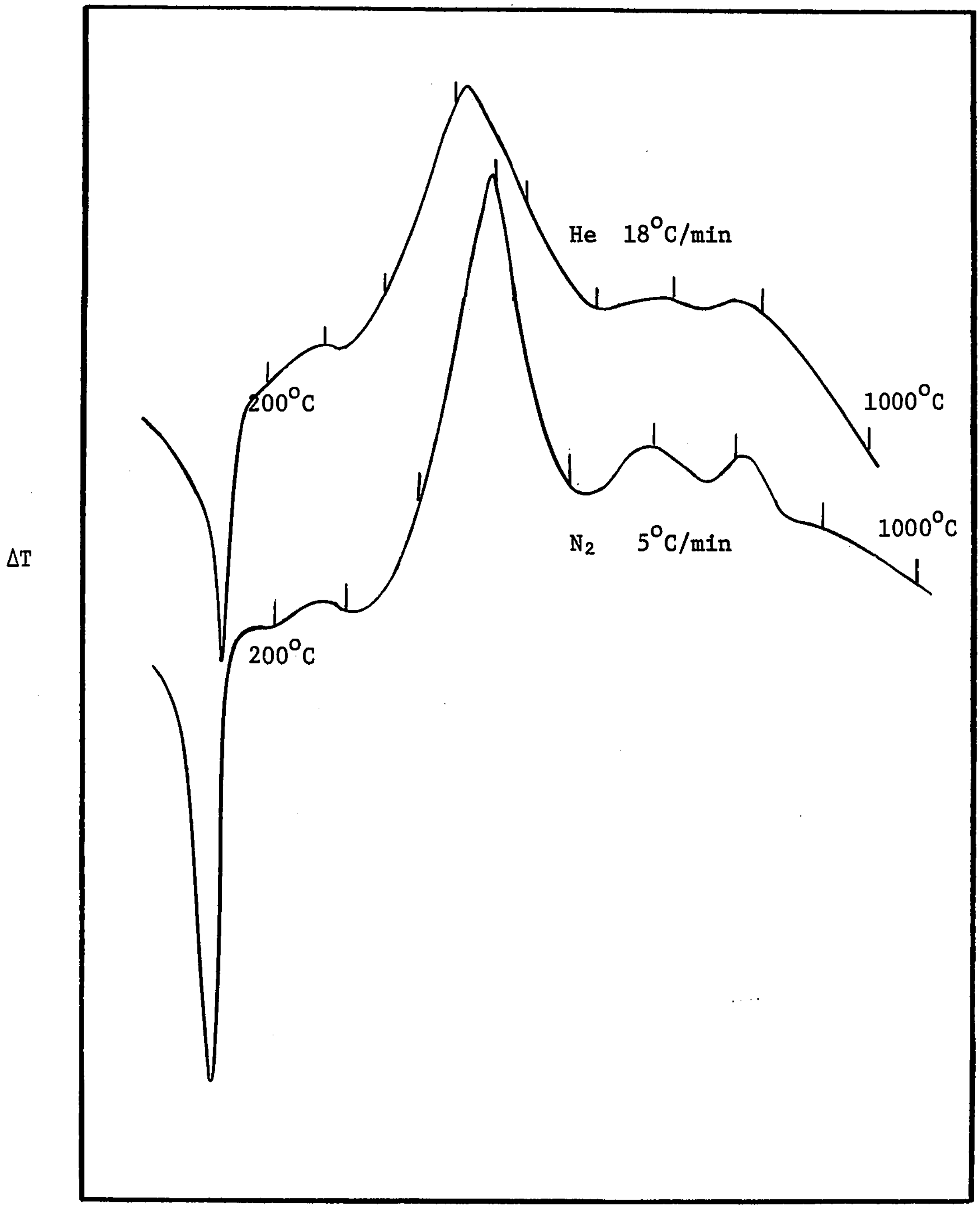
At temperatures above 1000°C graphitization of the carbon itself begins on a limited scale and increases with increasing temperature, being complete by about 3000°C (48, 41, 49, 17).

The temperature of evolution of a gas, or decomposition of a surface group, depends upon the nature of the functional group, i.e. type, bonding, proximity of other groups, location within a particle, etc. For instance, a carboxyl group is always connected by a single bond and is susceptible to heat; while a carbonyl can be incorporated within the aromatic matrix and be quite stable. The decomposition gases and their temperatures are definite products of the method of activation. Moist oxygen activation yields different products than that with dry oxygen. The decomposition atmosphere as well as the presence of other oxides also affects the products. A dry N_2 atmosphere over air-activated graphites showed a maximum in CO evolution at 675°C while wet N_2 over the same carbons shifted this maximum to 575°C (42).

For elucidation of the nature of surface oxides, samples of N:G (2:1) MA carbon were submitted to heating at a controlled rate with a flowing inert atmosphere in a Stone DTA (Differential Thermal Analysis) instrument. The samples were in the 100—300 mg range and Al_2O_3 was used as the reference material. Exotherms and endotherms at a given temperature are actually measured as temperature differences with Pt, Pt-Rh thermocouples. The DTA patterns of packed samples with helium and nitrogen atmospheres are shown in Figure 7. As the sample is heated adsorbed water is lost first and then four more peaks appear, representing at least four distinct changes due to the oxides, since graphite and graphitized blacks show no changes (55).

The large peak centered at 510°C appeared at a slightly lower temperature and was smaller with smaller, loosely packed samples; thus indicating that some of the atmosphere for the packed samples was not the inert gases, but rather some of the evolved product gas. This product gas was probably CO_2, which could re-react to form more surface oxides and CO (19, 20). Any one peak may be indicated at various temperatures for identical materials because of different heating rates, packing of samples, sizes of samples, moisture in carrier gas, and flow rates of the carrier gases, since the DTA instrument actually measures temperature differences and not energy absorbed or given off.

Product gases from subsequent runs were trapped at liquid nitrogen temperatures with the apparatus shown in Figure 8. These gases were then analysed on a mass spectrometer at the Helium Research Center in Amarillo, Texas. Air was a major contaminant in all samples because of 1) adsorbed air, 2) ease of trapping air when breaking connections at



Temperature, °C

Figure 7. Differential Thermal Analysis of N:G (2:1) MA in Flowing, Inert Atmospheres from 25°-1025°C. The temperature scale is not linear, and is therefore marked on the curves at 100°C intervals.

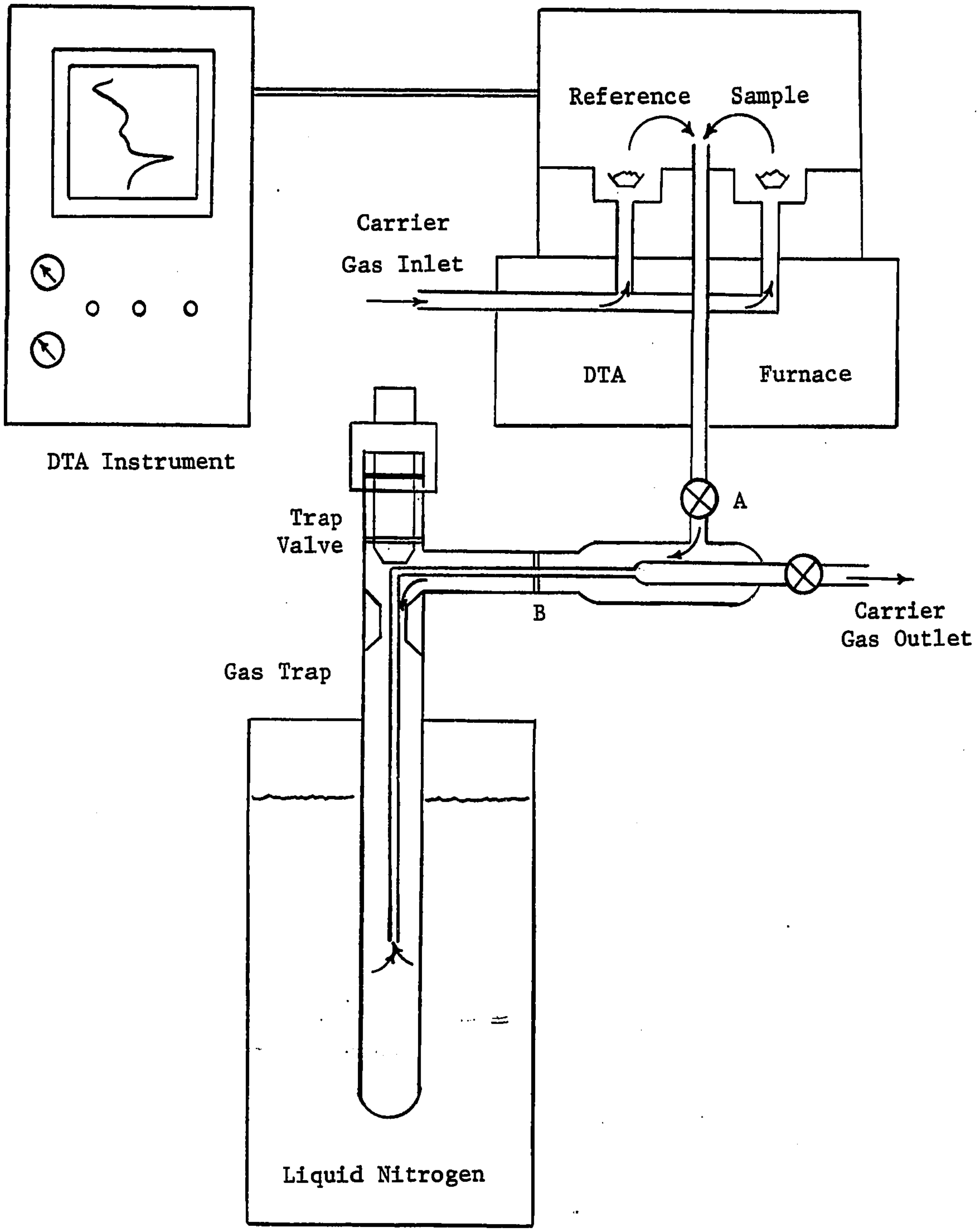


Figure 8. Diagram of Gas-Trapping Assembly Used with DTA of Carbon Samples. (1) The evacuated gas trap is attached to the system at point A. (2) The gas flows through the system as indicated by the arrows. (3) The trap valve is closed as the connection at B is broken and the small flexible line is withdrawn from the trap.

liquid nitrogen temperatures, and 3) the small possibility of leaks at the valve O-ring during the time delay between trapping and analyzing the samples (4-5 days).

The analyses of the product gases are presented in Table II. All gases were trapped with the previously described liquid nitrogen apparatus (except #88), with helium as the carrier gas, and the samples were all loosely packed.

Table II

Product Gases from DTA of N:G (2:1) MA

Sample #	Temperature Range of Evolved Gas	Partial Pressure of Gases H_2O	CO	N_2	O_2	CO_2	Ratio: CO_2/CO
88	25° to 450°C (trapped under Hg)	—	0.129	0.956	0.216	0.110	0.85
91	to 400°C	—	0.240	1.40	0.346	0.244	1.02
92	to 600°C	0.581	0.0734	0.762	0.154	0.446	6.07
93	to 925°C	0.265	0.111	0.501	0.130	0.553	4.98
90	to 900°C	0.604	0.111	7.396	1.39	0.0693	*

* Too much air contamination for accurate values.

The water analyses were completely unreliable because the amount of adsorbed water is so much greater than any of the other gases that droplets of liquid could be seen after the entrapment. Although the results are only qualitative because of mechanical difficulties and air contamination, it is significant that: 1) no H_2 was found as has been suggested for hydroxyl decomposition, 2) that most of the CO_2 is evolved between 400° and 600°C, corresponding to the large peak of the DTA pattern, and 3) that there is considerably more CO_2 for all oxide decomposition, indicating the predominance of carboxyl groups. The gases are evolved over ranges because of the expected distributional behavior from the physicochemical interactions of the groups, i.e. not all members of a group have the same bond energy.

The time and temperature lag between the sample and the gas entrapment was considerable because of the distance and low carrier-gas flow rate, thus causing considerable error in the evaluations. The traps were removed while the furnace continued to heat at 18°C/min and thus the lag was approximately 100°C. Considering that samples #88 and #91 are mainly from the first peak, the equal but low amounts of CO and CO_2 correspond to a weakly acidic carboxyl-carbonyl combination, i.e. the previously mentioned lactone. The DTA peak for this temperature range is quite small. Sample #92 represents nearly all of the large 510°C peak, mainly CO_2 evolved from carboxyl groups. Sample #93 should represent the total ratio of CO_2 to CO since it includes the CO of the last peaks from phenolic hydroxyl, carbonyl, and any ether-epoxy groups, but the ratio appears too high. Based upon the titrations a more realistic value would be nearer to 2, if phenolic hydroxyl does come off as CO and not mainly H_2O. It is not actually known how aromatic carbonyl or phenolic hydroxyl, i.e. ones attached to aromatic rings, would decompose but Boehm (50) stated informally that the carbonyl decomposed to CO_2 instead of the above mentioned CO, so if the latter is true then a carbonyl cannot be distinguished from carboxyl by this method.

The temperatures of the peaks agree quite well with literature values. Water (not adsorbed water) is evolved at lower temperatures and often peaks at 500°-600°C (42, 43, 44, 51). Wet chemical oxidations result in the first CO_2-evolving complex decomposing at 250°-350°C while gaseous oxidations have CO_2 peaks at 475°-675°C (41, 42, 47, 48). Very little if any true CO_2 is evolved above 750°C. The evolution of CO is reported at higher temperatures with peaks usually at 650°-750°C and some CO still evolving at 1000°-1200°C. The latter could explain why the final CO_2:CO ratio was higher than expected; not all of the CO was trapped by stopping at 900°C.

The almost continuous evolution of gases resulting from overlapping of decomposition energies of the oxides is well demonstrated by Figure 9. In this figure are the weight losses upon heating N:G (2:1) MA in various atmospheres on a Du Pont TGA (Thermogravimetric Analysis) instrument. After the loss of adsorbed water the weight reaches a plateau--the dry weight of active material. Upon further heating the weight continuously drops to 1000°C with only a minor change in slope at 650°-675°C. Carbons which have only one type of oxide, or at least a more selective group than those of mixed-acid treated charcoal, would show definite changes in weight upon heating (52).

Good correlations have been made of the total oxygen content of the carbons, usually determined by complete destruction of the material, with the oxygen given off as CO_2, CO, and H_2O, if adsorbed species such as moisture and air were removed beforehand (51). Methods of activation, degree of oxidation, and ash content influence this type of correlation greatly, so that for most carbons the agreement is quite poor.

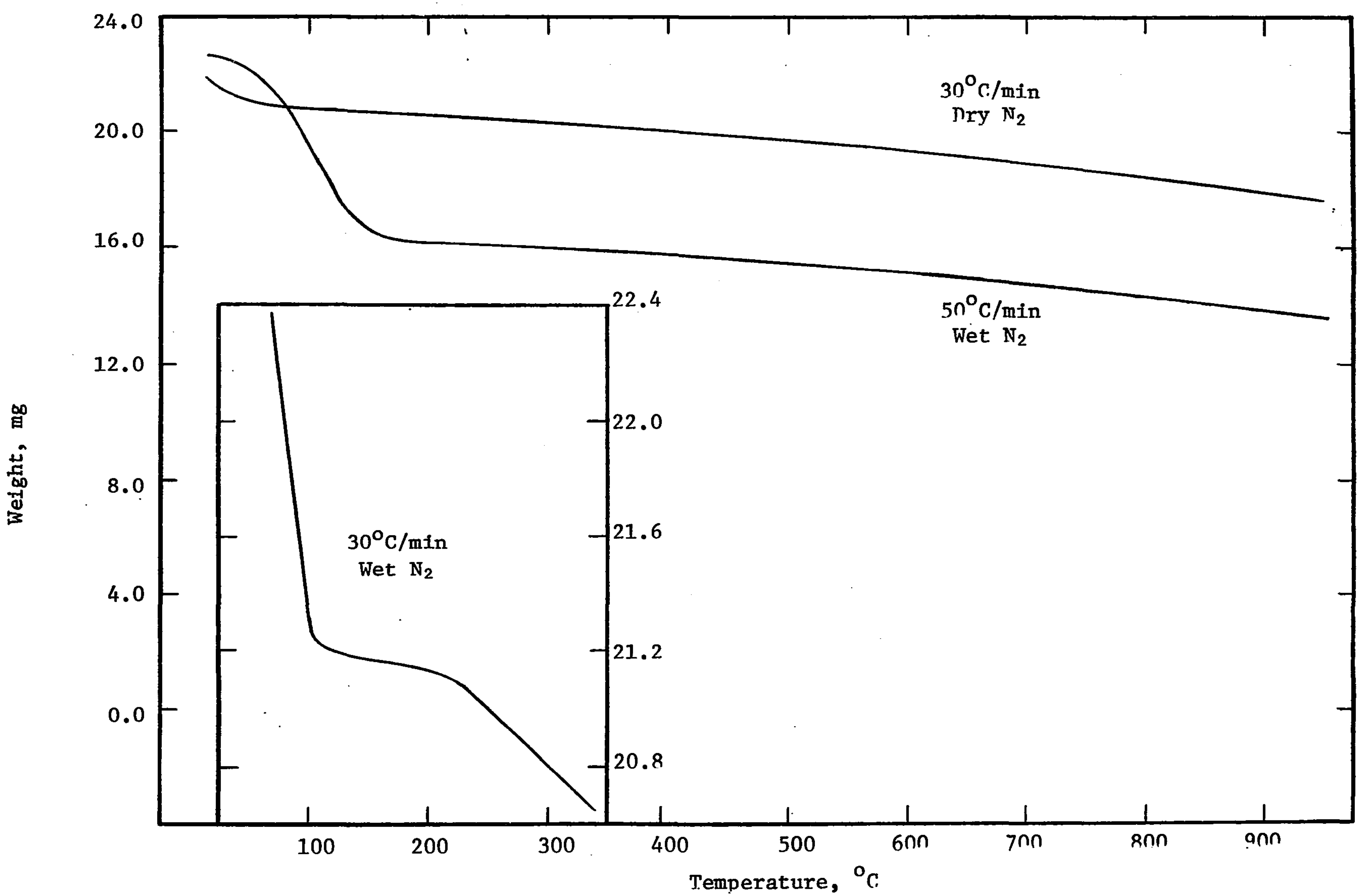


Figure 9. Thermogravimetric Analyses of N:G (2:1) MA in Various Atmospheres. Upper carbon sample was dry and the lower one wet, thus the greater weight loss. Insert shows the dry weight plateau in detail from a sample run on high sensitivity.

Better agreement is obtained with CO_2 evolution and macroscopic functionality of the carbon. Heats of wetting for H_2O (see section on Adsorption), initial adsorption of polar adsorbates, and acidity of the carbon as determined by base titration, correlate, within small errors, with the destruction and subsequent evolution of the CO_2-complex (12, 40, 47, 53). Puri's figures for acidity (by titration with sodium and barium hydroxide) of various blacks and activated charcoals compared very well with equivalents of CO_2 evolved on outgassing completely to 1200°C. The changes in acidity upon heat treatment to levels of 300°, 400°, 500°, and 750°C showed corresponding evolution of milliequivalents of CO_2. Likewise, the same treatment also altered the adsorption of water and methanol.

Upon complete outgassing to 1000°-1200°C the carbons are quite reactive, as to be expected (54), and begin to approach the properties of graphite as the temperature is further increased. DTA runs on natural graphites and highly graphitized blacks show no detectable endotherms or exotherms except those associated with the constituents of the "ash", usually SiO_2 and Fe_2O_3 (55).

Water Content of the Carbon

In the evaluation of macroscopic properties of the carbons problems arise as to what to use as a base point in the determinations. Since the carbons are not a solid with a definite lattice or crystallinity the use of molecular weights or anything related to a fixed species is purely nonsense. The obvious reference point for such an "amorphous" material is weight. Even this base has limitations, since many properties are functions of porosity, particle size, and/or surface area (which itself is a function of porosity).

With many of the experiments, if not all, the determination of amount of active material (i.e. the carbon only) by weight was not an easy chore because of the ever present problem of water adsorption. The carbons no doubt had some water content when received but this was soon drastically altered by the activation process. The charcoal-graphite was activated in an aqueous medium (the mixed acids: H_2SO_4-HNO_3), washed with copious amounts of water, and in the electrode fabrication, dispersed into an aqueous slurry before being placed in the cells and thus contact with flowing aqueous salt solutions. The "wet cake", i.e. the carbon after activation and washing, was often more water than carbon, even after dehydrating with suction filtration. Determinations on wet cakes have placed the water content as high as 54% by weight. The carbon in this case held up to 117% of its own weight in water. It should be pointed out that a wet cake was not in equilibrium with water vapor and was holding some "liquid" water.

The amount of active material was determined by a "per cent solids" method. 1) First, the wet cake was chopped into small particles with diameters no larger than 2 mm. 2) Then the finely divided carbon was placed in a humidity chamber at 25.0°C and allowed to come to equilibrium with the water vapor at this temperature, a process involving three to four weeks. (The material used in experiments, such as the titrations, was this carbon which had been equilibrated with water vapor.) 3) Samples were removed in closed containers and immediately weighed. 4) Some of the samples, usually every fourth one, were placed with the container open in an oven at 110°-120°C to dry. 5) The drying samples were removed at daily intervals, with the containers closed immediately upon removal from the oven, to cool in a desiccator and be weighed. The daily weighings were continued until the drying carbon reached a constant weight, within ±0.05%, for three consecutive weighings. As to be expected, the majority of the water was lost the first day of drying; the weight then decreased slowly over the next few weeks. The attainment of the constant weight plateau is shown in Figure 10 for three samples from the same batch.

It will be noticed that although the samples each reach a constant weight plateau it is not the same plateau for all. This is the reason that so many per cent solids samples are taken during an experimental set-up. The carbon is in equilibrium with water vapor when the first sample is removed but with the opening and closing of the humidity chamber for sample removal the equilibrium is disturbed. Rather than wait for equilibrium to be completely re-established the actual water content is determined by removing portions for per cent solids determinations at the same time as experimental samples are removed.

Since care was exercised in this procedure, it is obvious from the above statements that some of the water equilibrating is quite rapid. It has often been observed that when a "wet" sample is left open to room humidity on a balance that major changes occur in a matter of a few minutes. The rapid equilibrating of water vapor supports the hypothesis that the water uptake is a result of physisorption, not chemisorption.

The variance of per cent solids values was usually ±0.3—0.5% for 10—12 samples removed over an hour's time. Therefore, in practice, the

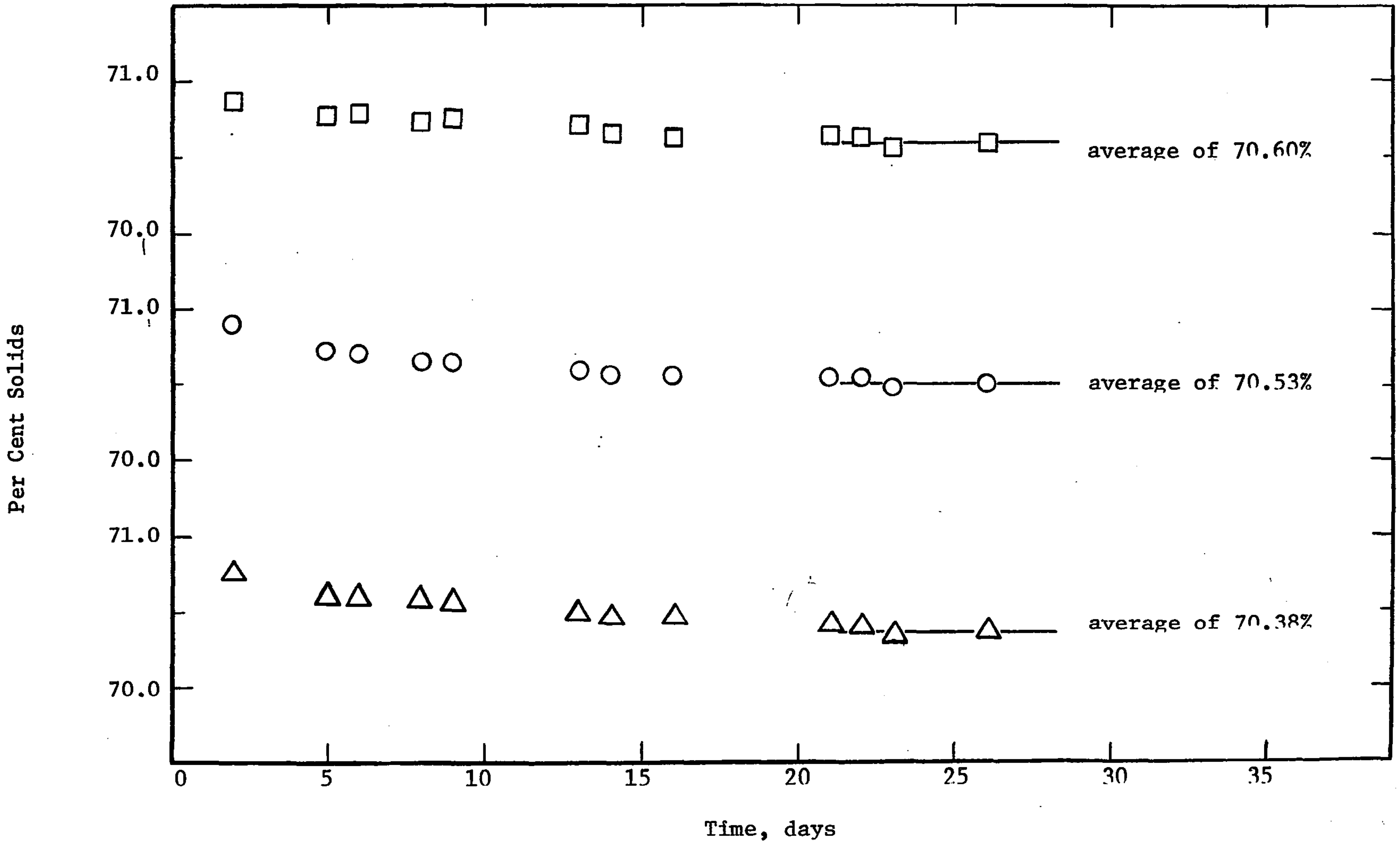


Figure 10. Per Cent Solids of Drying Carbons with Time. The per cent solids of carbons equilibrated with water vapor as determined by daily weighings of the carbons after drying at 110°–120°C. The carbon is considered to be dry when three consecutive weighings vary no more than ±0.05% of the weight.

per cent solids values were used as three significant figures. The actual weighings were considerably better than that; for example, a two gram sample of wet carbon can be weighed to ±0.05 mg but any per cent solids value is the result of three weighings, so a more realistic error was ±0.3 mg. Thus the weight of the usual carbon sample was known to five significant figures, or an error of about ±0.02%.

Adsorption of water. The adsorption of polar species such as water occurs by at least two mechanisms. As the relative pressure is increased the species is first adsorbed as individual molecules on surface oxides, most likely by hydrogen bonding. More adsorbate is taken up on the solid in the form of extensions from the previously adsorbed molecules by lateral hydrogen bonding; thus the oxides give rise to "islands" of adsorbate. The islands may locally be thicker than a monolayer but may not extend uniformly over the surface. In fact, if the carbon is highly graphitized with well developed aromatic sheets the basal planes may only be spotted with a few molecules, which are weakly held by some sort of bonding with the pi electrons of the aromatic rings. As the sheets of adsorbate extend with increasing relative pressure, capillary condensation occurs in the pores of the solid. The latter has actually occurred over the entire pressure range but only becomes significant when the temperatures and pressures approach those of liquefication. (It might also be noted that, except for pores of the size of the adsorbate molecule, capillary condensation may actually be initiated by adsorption at local oxides in or near the pores. In fact, Dubinin considers that the surface oxides line the walls of the micropores (5).) Heats of adsorption are higher for the polar species than for non-polars such as benzene; it is 10—13 kcal/mole for H_2O. Adsorption on carbons is reviewed by Dacey (6), Culver and Watts (7), and Kipling (56).

The presence of surface oxides on carbons increases the total amount of polar species adsorbed. Even more dramatic is the effect upon the adsorption isotherm at low relative pressures of adsorbate. In the absence of surface oxides water adsorption is not significant until high P_i/P_{vap} (in some cases, 0.8), while in the presence of surface oxides adsorption is not only significant at very low pressures, but may actually constitute from 25—50% of the total amount adsorbed (6). Further proof of the importance of the oxides in adsorption are two very good linear correlations of heats of wetting or immersion, with oxygen content of the carbon material by Kraus (57) and Puri *et al.* (53). Kraus also points out that there is about 50 $ergs/cm^2$ (of surface area) difference between an oxygen-free surface and one with oxides for the heat of immersion of a polar species. For a non-polar, such as *n*-hexane, there is no difference, i.e. the surface oxides play a very small role in the latter adsorption.

The heat of adsorption for H_2O decreases with increasing relative pressure, from a maximum at zero pressure (7), and finally approaches the heat of vaporization for water at a pressure which is consistent with the lateral hydrogen-bonding and beginning of capillary condensation concept.

Puri modifies his correlation with oxygen content and states that rather than the total oxygen content, it is only that oxygen which is involved in a complex capable of being decomposed to CO_2 by heating to 750°C. This CO_2-complex, which is most likely a carboxyl group, constitutes 92—94% of the bound oxygen when activation is by O_2 or NO_2 at 400°C. As previously stated, decomposition of all of the oxides, i.e. outgassing, can be accomplished by heating the carbon in an inert atmosphere to 1000°-1200°C. Carbons which have been heat treated to this level adsorb a very much smaller amount of polar adsorbates and the energy of adsorption is approximately that of vaporization, i.e. the adsorption is by a capillary condensation type mechanism. This has been reported for H_2O, CH_3OH, SO_2, CO_2, and NH_3, but the drastic reduction in total amount adsorbed with heat treatment is not noticed for non-polars, such as C_2H_2 (7, 53).

Puri (47) has demonstrated the correlation with surface oxides very well by partial outgassing of the carbons at several temperatures up to 1000°C, measuring the correspondingly evolved CO_2, and submitting the heat-treated carbons to water and methanol adsorption. Outgassing to 300°C reduced the total water adsorbed by more than 20% and further treatment to 500°C reduced it at least another 20%. The heat treatment greatly alters the shape of the adsorption isotherm, reducing the amount adsorbed at low relative pressures with increasing treatment temperature up to 750°C, where the mechanism involving the CO_2-complex is terminated.

Heat treatment in H_2 atmospheres has the same effect as in an inert atmosphere, but in the H_2 situation the oxides may simply be replaced while in the inert atmosphere some graphitization occurs and the replacement of oxides is not reversible without an activation process that destroys part of the carbon matrix (47, 58)

Zettlemoyer and Narayan (59) report the same type of correlation with polar adsorbates and heat treatment for silica. Water adsorption on silica is by physisorption with silanol and siloxane groups on the surface, with energies of adsorption of approximately 12 kcal/mole.

Water adsorption on a carbon activated by the mixed-acid treatment (concentrated HNO_3: concentrated H_2SO_4 (1:2)) is reported by Kiselev *et al.* (9) to be increased by a factor of 4—5 over the untreated material although the surface area (148 m^2/g) of the carbon was not changed by the activation. The total water adsorbed was 16 mmoles/g carbon for an unspecified temperature and the oxygen content was 14%. The adsorption of *n*-hexane and benzene on the activated black was almost identical with that on the as-received material and also to that of the material when heat treated to 1700°C, about 1.5 mmoles/g for both. The above figure compares to the 23—24 mmole H_2O adsorbed per gram dry carbon for mixed-acid treated charcoal-graphite prepared on this project. The adsorption of polar species on N:G (2:1) MA is presented in Table III.

Table III

Adsorption of Polar Molecules on N:G (2:1) MA

Adsorbate	$\frac{\text{mmole adsorbed}}{\text{g dry carbon}}$	$\frac{\text{mmole adsorbed}}{\text{meqv total acidity}}$
Water	23—24	11.4
Methanol	9.4—9.7	4.6
Ethanol	6.8—7.1	3.4

The figures in the last column are only an approximation to indicate relativeness, since the total acidity was determined by hydroxide-ethoxide titrations, which never actually reached a precise limit but only approached one. The water isotherm has been measured on dry, untreated Norit A (60) at 25°C and the charcoal adsorbed only 7.5 mmoles of water per gram of dry material.

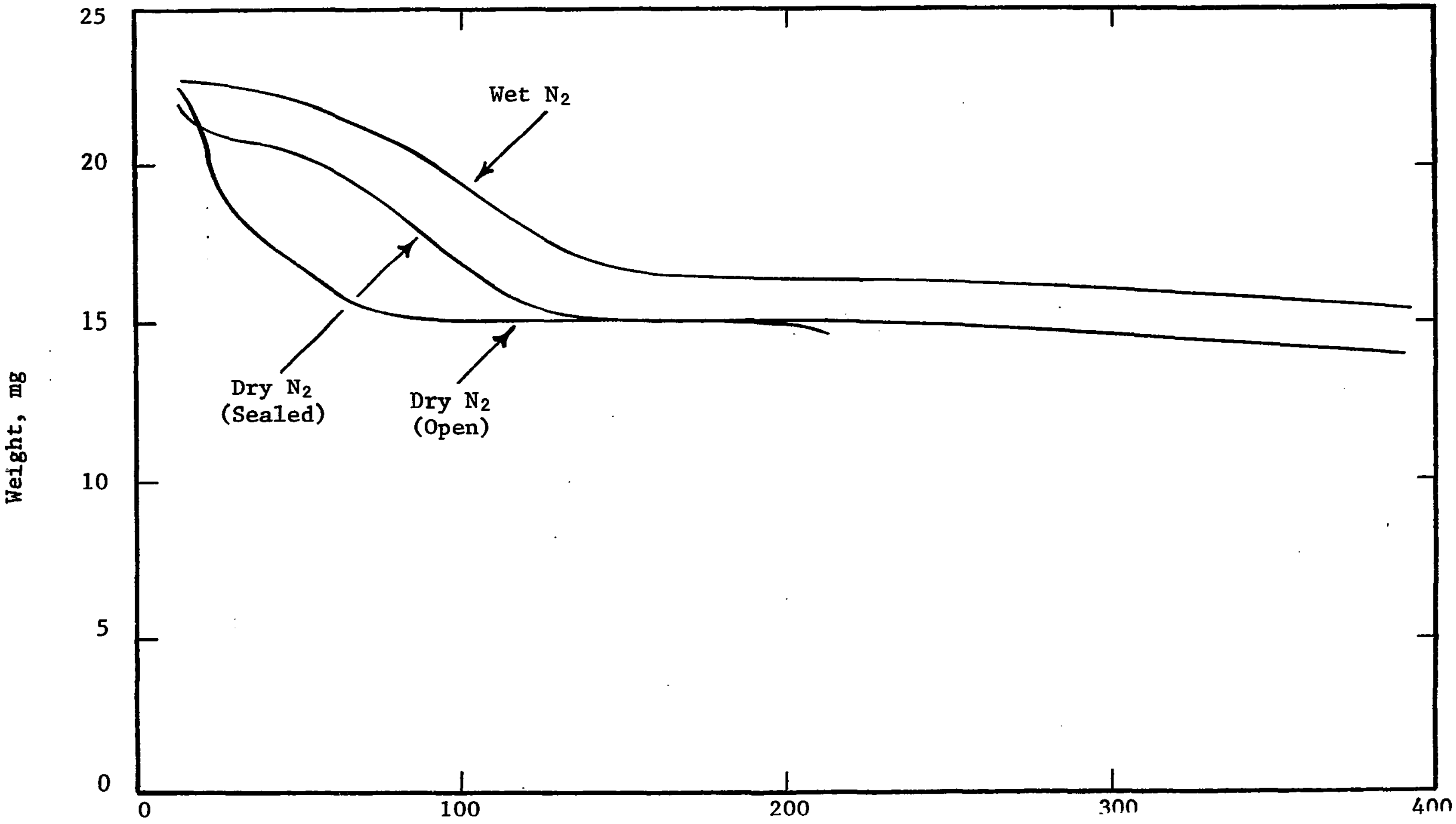
The drying procedure used to determine amount of active material on this project is usually reliable within ±0.3%. Considering the difficulty involved in obtaining a reproducible carbon this figure is quite acceptable. The method of using a wet instead of dry carbon for experimental samples is obvious from the above discussions of adsorption. A dry sample introduced to solutions, such as those used in titrations, adsorbs some of the solvent and alters the initial and final concentrations, leading to false conclusions about ion-uptake. A carbon which has been equilibrated with water vapor before introduction to liquid solutions will have adsorbed an amount very nearly equal to that which would be associated with the carbon when in the solution, although water molecules may change relative positions and local interactions will change.

Drying temperature. The use of 110°-120°C as the drying temperature has troubled some who contend that part of the water is chemisorbed and remains on the carbon. Since the mixed-acid treatment is such a severe oxidation method, it is highly unlikely that there are many active sites left to react with such a weak agent as water to form initial oxides directly on the carbon. It does appear that a part of the water is involved in hydrating a few of the surface oxides, such as converting carbonyl to phenolic hydroxide, because the desorption isotherms exhibit a hysteresis which is permanent, i.e. not all of the water is desorbed at a given temperature just by lowering the pressure (47, 9). Kiselev was only able to remove all of the water from his mixed-acid treated sample by heating to 100°C. The important point is that he was able to remove all of the water with a temperature close to the boiling point, i.e. the water was physisorbed, not chemisorbed.

Samples of N:G (2:1) MA were submitted to thermogravimetric analysis on a Du Pont TGA-DTA instrument in order to clarify the point of drying temperature. As shown in Figure 11 the water was lost at temperatures near the boiling point, actually below 100°C with dry nitrogen flowing over the sample. The temperatures for the wet sample are deceiving since it was heated at 50°C/min, a high rate which shifts all points "up" temperature. Another sample which is not shown, also in wet nitrogen, but heated at 30°C/min lost all water by 120°C.

The effect of the humidity of the surrounding atmosphere is obvious again, indicating physisorption, which is a function of relative water pressure. Dry samples adsorbed 7% by weight of water from the wet nitrogen streams even in the short time it took to set up the samples. All water is lost by heating a sample in flowing dry nitrogen to only 80°C.

Differential thermal analysis (DTA), in which temperature differences are measured between a sample and reference (usually Al_2O_3) as both are heated at a constant rate, also showed that all water is lost by 110°-120°C. The endotherm from water loss is presented in Figure 12. (See also Figures 7 and 9 in Thermal Decomposition section.) Again, all water is removed by 120°C as was shown in the TGA experiments. Per cent solids determinations on the same samples used in the TGA experiments agreed quite well with calculations made from the graph.



Temperature, °C

Figure 11. Thermogravimetric Analyses of Wet Samples of N:G (2:1) MA in Various Atmospheres. The samples were previously equilibrated with water vapor at 25°C. The upper sample was heated at 50°C/min and the lower two at 15°C/min.

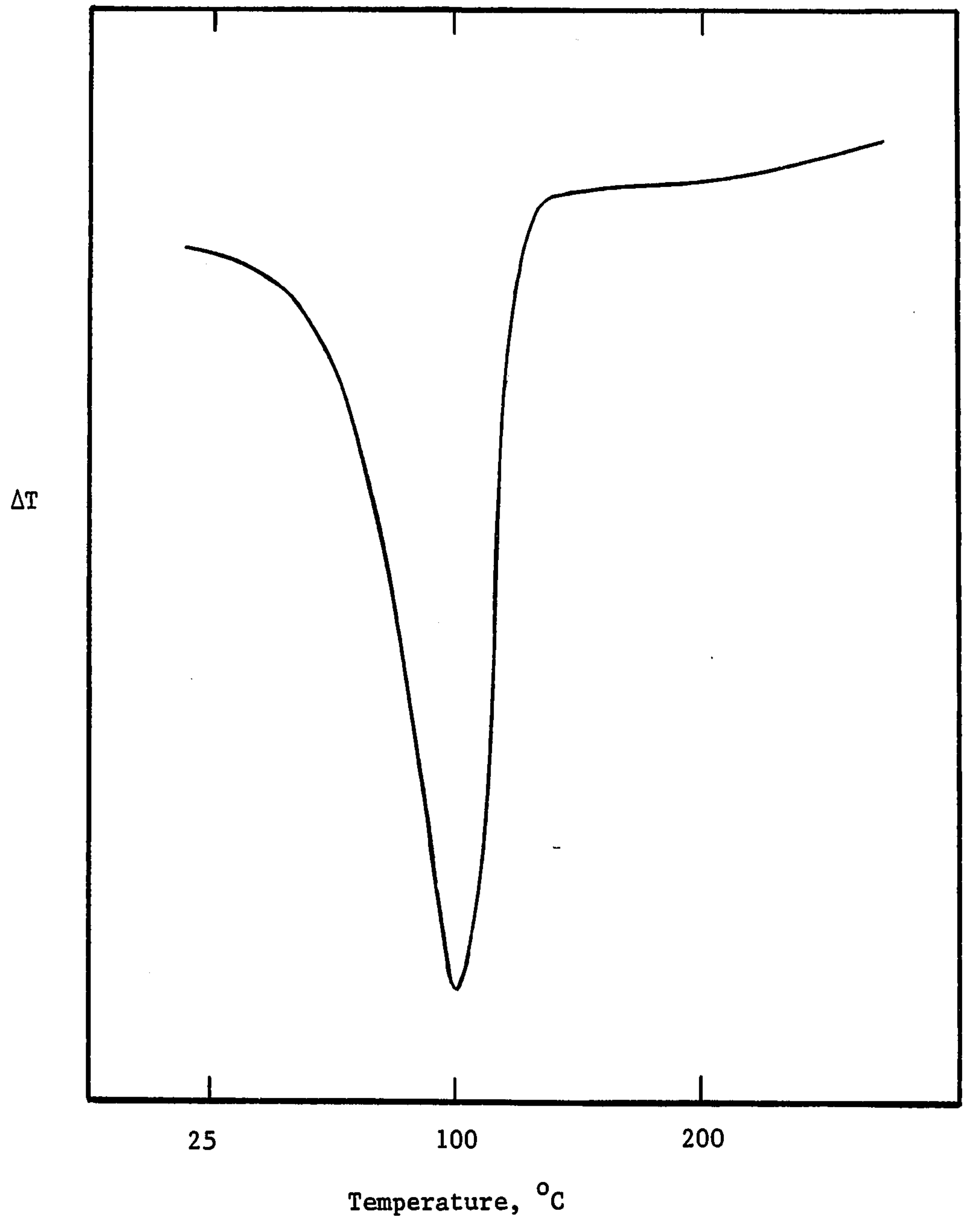


Figure 12. Water Endotherm from DTA of N:G (2:1) MA. The carbon had been equilibrated with water vapor at 25°C. The sample was heated at 5°C/min in a flowing nitrogen atmosphere with Al_2O_3 as the reference material. The temperature scale is not linear.

Thus, when the charcoal-graphite is activated and oxides are created on the surface, water is easily adsorbed on the carbon. This water is held by some combination of weak "physical" bonds with hydrogen bonding being the most important. The energies involved are equal to those of liquefication-vaporization at high humidities, obviously because the water coverage is quite extensive[1] and it behaves much like a liquid. At very low humidities the interaction is more on an individual basis between molecules of water and specific oxides. The adsorbed water can be removed and the amount of active material determined by heating in an oven at 120°C for long periods of time.

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[1] Approximate calculations indicate an average of one molecule of H_2O per 1-2 A^2 of surface area for N:G (2:1) MA.

III. DEMINERALIZATION WITH N:G (2:1) MA ELECTRODES

Methods and Mechanics of Demineralization

Electrode Fabrication

In the years previous to 1964 several hundred demineralization runs were made to test a good number of carbonaceous materials as electrodes. The great majority of the as-received carbons, including blacks, charcoals, and graphites, exhibited more capacity for cation removal than anion. Only a few had good cation capacities and none had high anion capacities. Carbolac 1, Nuchar C-190-N, and Norit A were the best for cation removal when paired with Ag, AgCl electrodes.

Activation, treatment, and dispersion studies were done to improve the capacities and physically stablize the electrodes. The activation by the mixed-acid method improved the cation capacities by factors of 2-5 times and reduced the anion capacities to very low values, 1-3% of the final cation level. A large number of the studies were devoted to developing a carbon electrode with a comparable capacity for anions, including high temperature ammonia treatment and amine activation in hopes of imparting quaternary ammonium groups to the carbon. Anion-responsive carbons were prepared, resulting in adsorption of anions to 0.3 meq/g carbon, but these did not compare with the cation-responsive electrodes, which were four times higher (61).

Much work was also done on electrode preparation, cell design, carbon slurries, and electrode backing materials. After all of the above testing and evaluation it was decided that an electrode consisting of two parts by weight of finely pulverized Norit A charcoal (N) with one part Dixon's Air Spun 200-10 graphite (G), activated with two volumes of concentrated H_2SO_4 mixed with one volume of concentrated HNO_3 acid (MA) was the most reliable, physically stable electrode material with a good cation capacity (62).

This activated carbon, designated as N:G (2:1) MA, is washed until the decantate is $SO_4^=$ free and has a pH of 3.5—4.0. It is dispersed with 2-3 ml of water per gram and 5% by dry weight of tannic acid, then stirred to smoothness with a spatula. Usually enough carbon is used to make 4-6 electrodes at one time. The silky smooth dispersion is allowed to stand overnight in a 100% humidity chamber and then the excess acid is neutralized with NH_4OH until the carbon slurry is above pH 10. It is allowed to stand again in a wet atmosphere to assure that all acid is neutralized.

The smooth-appearing dispersion is then worked with a spatula into a previously weighed 2" x 6" piece of porous, calendered Dacron paper. Excess carbon is removed and the electrodes are dried. Dacron paper was finally decided upon as the backing material because of its porosity, thinness, and physical stability. Earlier studies have shown that the slurry water content and tannic acid have no effect upon electrode capacity (61). The graphite was added to lower the resistance of the electrode and to improve physical stability of the carbon on Dacron paper.

After the electrodes are dried the overall thickness is measured with a dial gauge; the resistance through the electrode is checked with a Wheatstone slidewire bridge; and the electrode is weighed to determine content of active material. An ordinary electrode has a thickness of 0.5—1.0 mm, a resistance of 3—13 ohms and carbon content of 1.3—2.3 grams (63).

Cell Construction

The dry carbon electrode is incorporated into a demineralization cell as shown in Figure 13. The carbon and silver electrodes are laid on their respective graphite backs and held in place, in gasket fashion, by polyethylene spacers of the same approximate thickness as the electrodes. The electrodes are then pressed gently against the graphite backs by the PVC screen of the center spacer. The screen allows solution to flow up the cell and reach all of the electrode area while still physically holding them firmly. The cell is then pressed together in sandwich fashion and secured by bolting the Plexiglass blocks to each other, with a resulting interelectrode distance of 1-3 mm.

The graphite backs are used as corrosion-resistant electrical connectors. As pressed graphite they are quite porous and have to be sealed on the outside with an impervious layer of Pyseal, a high-melting sealing wax. Into and through the graphite connectors are threaded two pieces of nylon tubing with 1/4" OD and 1/8" ID, one just below the carbon electrode with the other just above. Solution enters through the nylon port at the bottom and flows up the cell, parallel to the electrodes, and out the upper port. Electrical connections are made by brass jack plugs

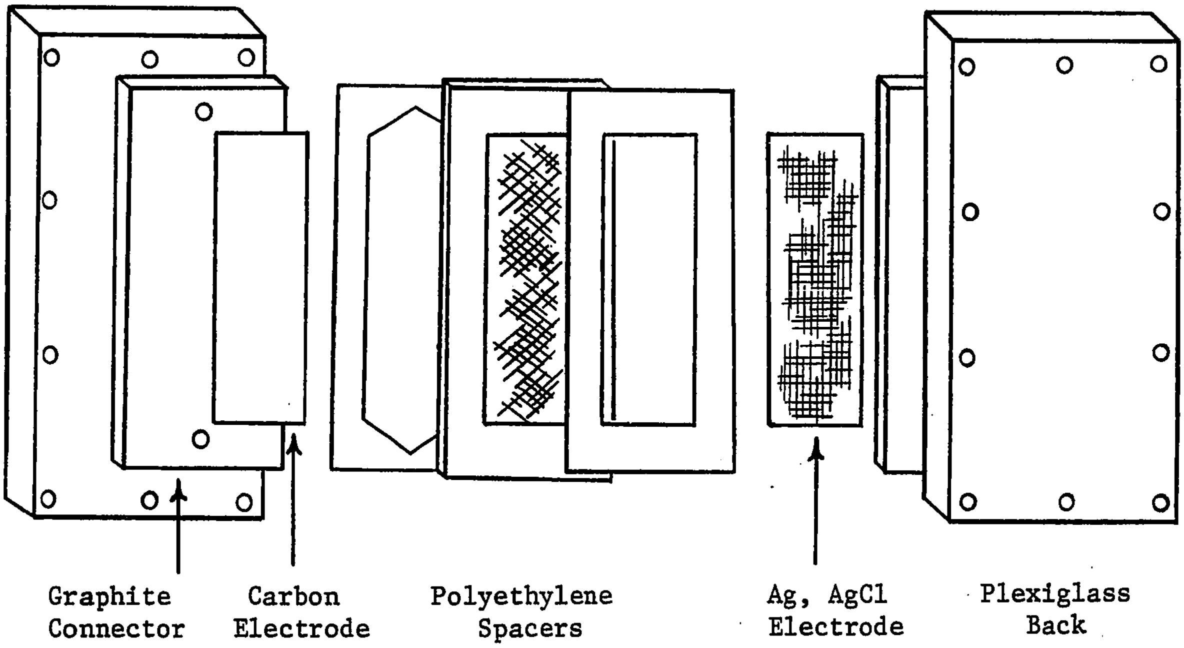


Figure 13. A Disassembled View of the Demineralization Cell. Solution enters through the bottom port in the graphite block on the left and flows up the PVC screen of the center spacer and out the upper port. The graphite blocks are used as electrical connectors to the 2" x 6" carbon and silver electrodes, and the entire cell is held together by bolts through the Plexiglass backs.

threaded into, but not through, the 1/4" thick graphite. It is quite important to have the inner surface of the graphite planed smooth and flat to prevent leaks.

The silver, silver chloride electrode is prepared from silver wire mesh by depositing a uniform layer of the chloride from electrolysis of HCl-NaCl.

To prevent air contamination in the oxygen-free experiments the entire sandwich of graphite backs, electrodes and spacers was sealed with Pyseal on all outside surfaces.

Slight modifications, such as the above, were also made in other experiments. In cases involving high hydroxide concentrations, e.g. above pH 12, the PVC-polyethylene spacer was replaced by an appropriate all polyethylene spacer, because of attack on polyvinyl chloride by hydroxide.

Accessory Equipment

The glass manifold and the glass inlet tubing are heat-sealed to the nylon tips by heating the tapered glass ends and forcing them into the nylon tubing. The nylon is softened and upon cooling an air-tight joint is made. Thus with the use of glass tubing throughout the rest of the system the solutions are in contact with pyrex, Teflon, and nylon until entering the cell.

The solutions are circulated by Teflon-lined Beckman Solution Metering Pumps of the piston-valve type pulsing every 15 seconds. The flow rates were usually in the 110-120 ml/hr range and were set at a constant value by mechanically adjusting the piston stroke length until the desired flow rate was obtained. The constant flow rate was usually reliable to ±0.2 ml/hr as determined by measuring the volume of effluent over a specified time. The flow rate often stayed at the preset value for weeks within ±0.5 ml/hr before readjustment was necessary. In practice the flow rate was measured for each run.

The cells, electrodes, and some of the electronic instrumentation were maintained at 25.0^{o} $\pm 0.1^{o}C$ in a 30 cu ft air bath. The room was maintained at 21^{o}-$25^{o}C$ and in combination with a water-cooled blower within the bath acted as the heat sump. The instrumentation radiated a constant amount of heat and regulation of the temperature was by a mercury thermoregulator, relay, and 250 watts of incandescent light bulbs. Two fans, one operating at 1700 rpm, maintained circulation throughout the bath.

The saline solutions, usually 0.03 N NaCl, were kept in sealed glass reservoirs with the desired atmosphere controlled by bubbling gases continuously up through the reservoir. The system was sealed from atmospheric gases at all practicable points and the only possible air leak was at the stems of the valves and piston in the pumps. In some early experiments the entire pump and cell were sealed within a "dry box", located inside the air bath, to determine the influence of oxygen (see section on pH studies). For later runs the entire solution system was made of glass and the effluent gas stream from the nitrogen-saturated reservoir was directed into an enclosure around the pump piston and valves in case of possible leaks.

Two complete reservoir systems, one for nitrogen-saturation and the other for oxygen- or air-saturation were continuously in operation. The nitrogen gas was passed through a KOH-pyrogallol scrubber to remove any traces of oxygen as shown in Figure 14.

Because of the long times needed to condition a cell, both electrically and with respect to the feedstream and its dissolved gases, there were often three to five cells in operation at one time, each with its own pump, timer, switches, and power supply. Because of the expense involved only one set of monitoring units was used.

Effluent Monitoring

In the earlier years of this project the effluent from the demineralization cell was monitored by small custom-made platinum electrodes and conductivity measurements. The conductivity recordings, converted to sodium chloride concentrations by appropriate calibrations, were quite reproducible and adequate for evaluation of electrode testing. When the studies on individual ion removal began it became apparent that there were problems involved with potential differences. The cell is always grounded at one electrode during operation and this constitutes a difference in potential between the cell and the conductivity electrodes, thus causing a current to flow along the salty effluent solution. The previous method of monitoring was deemed no longer adequate and design changes based upon specific-ion electrodes were begun.

The acquisition of specific-ion electrodes was not accomplished until late spring of 1967, but the other major concern was reliable, steady, meter-bridges to convert the electrode potentials to suitable outputs that could be continously recorded. The purchase of the Orion 801 digital pH meter was the first step in getting reliable measurements of individual ionic concentrations without removing samples of the effluent but measuring in the stream itself.

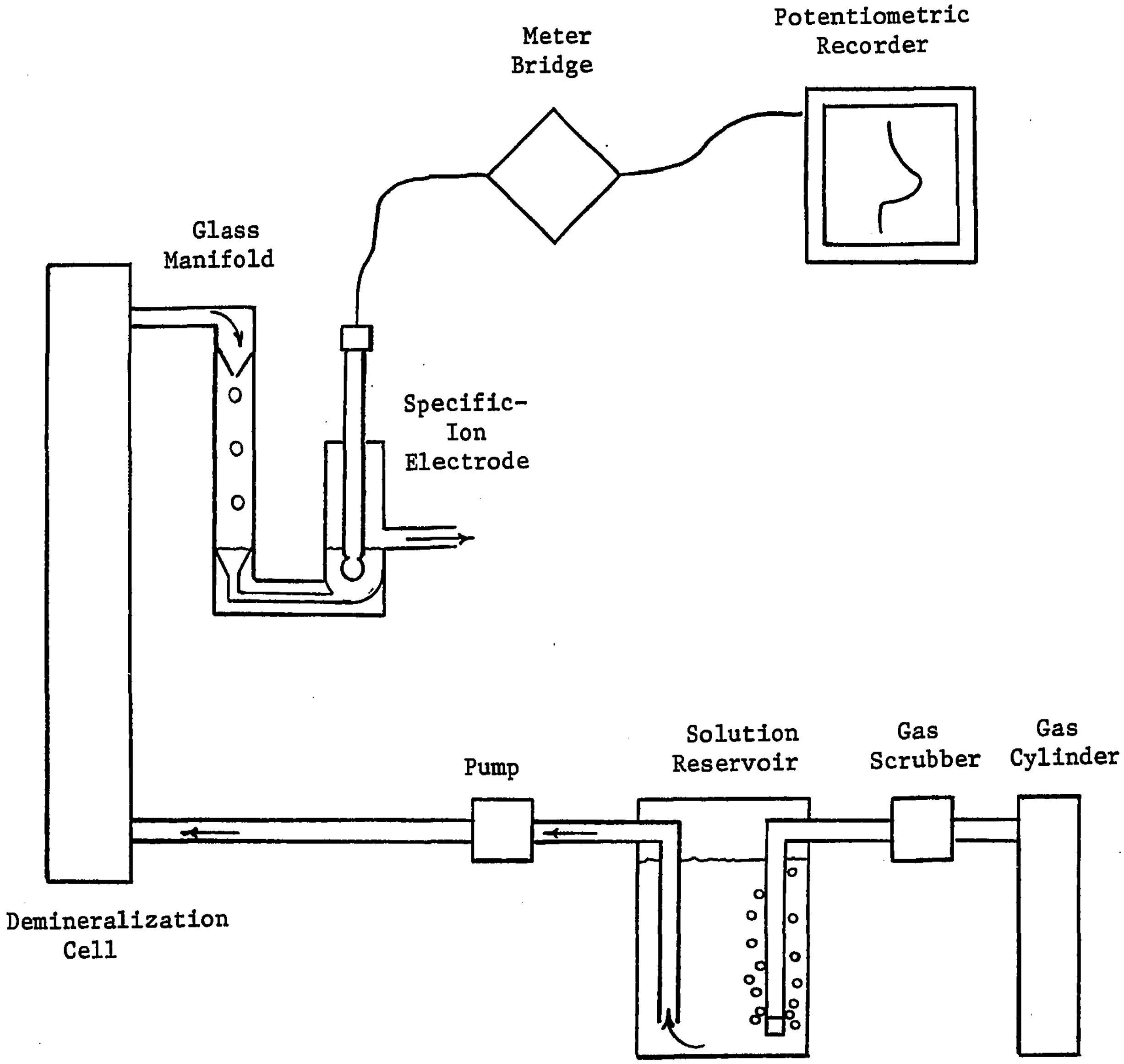


Figure 14. Schematic of the Cell and Accessory Equipment. Only one of three specific-ion-electrode-bridge-recorder systems is shown. The arrows show the saline solution flow.

A glass manifold was designed to hold the specific-ion electrodes for measuring concentrations with as little hold-up volume as practicable while physically breaking the effluent stream to isolate the electrode potentials from the cell potential, thus eliminating extraneous currents. It was also desired to isolate the monitoring electrode pairs from one another to eliminate KCl contaminations from the calomel reference electrodes as well as any stray currents that might arise. A parallel arrangement of close fitting tubes with dripping tips and receptacles was finally constructed after a few design problems. Drawings of the glass "cow", as it was fondly called, are shown in Figure 15.

The hold-up volume is only 10—12 ml of solution when all electrodes are in place and the time delay is about 90 seconds. The glass manifold and electrodes function quite well with the only disadvantage being that the flow rates are so low that the electrodes are not bathed as vigorously as needed. This results in a somewhat slower response to changes than desired.

Figure 14 is a diagram of the cell, glass "cow", electrodes and associated electronics, and the accessory equipment to control the dissolved gases in the salt solutions.

Specific-ion electrodes and related electronics. The pH probe was a Sargent-Jena minature combination glass-silver, silver chloride electrode used in conjunction with a high impedance bridge. The earlier-used bridge was a Sargent Recording Adapter, but the drift in this instrument was too large and too erratic for the continuous use that was needed, and necessitated recalibration every few hours. A custom-made, dual channel bridge, based upon a differential input operational

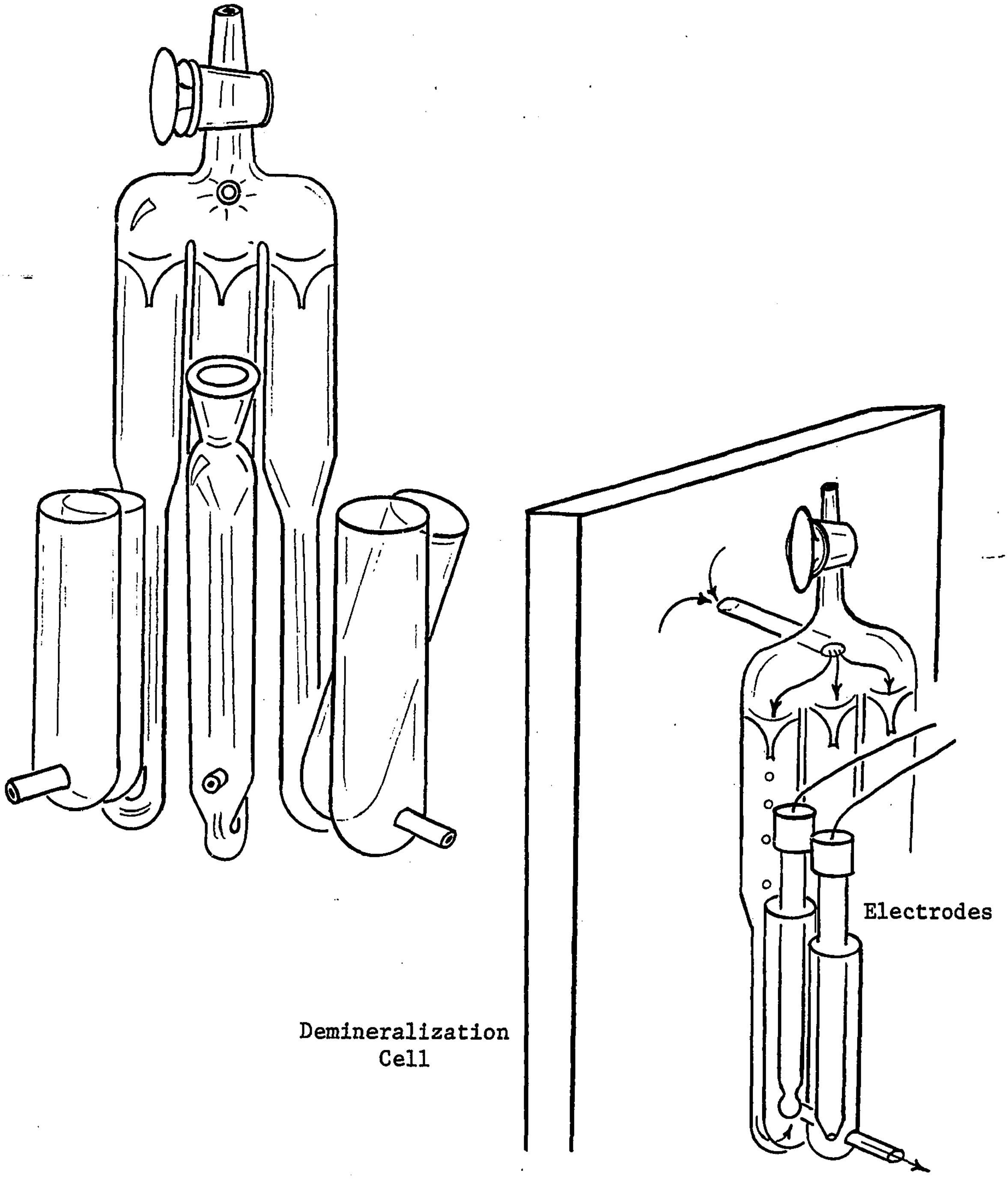


Figure 15. The Glass Manifold and Dripping Chambers Used to Divide the Effluent into Three Isolated Streams. The solution departs from the cell and enters the manifold at the top rear where it is split and falls as droplets from the three tips. Specific-ion electrodes are located in the front vertical tubes to monitor the three streams separately. The stopcock is used to clear air bubbles from the manifold.

amplifier in conjunction with the usual electrometer tube and a feedback circuit, was designed and built to provide a steady, reliable potential converter. This pH adapter bridge was quite linear and precise and gave satisfactory performance. The output was continuously recorded on a potentiometer type recorder after calibration with commercial buffer solutions reliable to ±0.02 pH unit; thus giving an overall precision for the full pH scale of ±0.05 pH unit. The usual range used was from pH 3 to 11, but for special runs other ranges were used.

Before the acquisition of the specific-ion electrodes the sodium of the effluent was determined by taking timed samples of the stream, diluting, and analyzing on a Coleman flame photometer; thus correcting the conductivity values for the other ionic species present. The *in situ* measurement of sodium ion was accomplished with a Corning NAS 11-18 sodium ion electrode, which operates on the same principle as an ordinary glass electrode, i.e. the potential of the membrane (glass) surface changes with respect to the standard internal solution because of ion-exchange type reactions with the changes in concentration of the specific ion within the measured solution. The external reference electrode was a saturated calomel electrode. The electrodes' output was usually sent through the mv section of the Orion 801 digital pH meter, and then to a Beckman potentiometric recorder. The latter two instruments are considered to be some of the best available and were used for sodium ion measurements because of their sensitivity and solid-state reliability. The stated capacity of a carbon electrode is actually the measurement of sodium ion removal since it is cation-responsive and therefore paired with the ideal chloride electrode, the silver, silver chloride; thus the reason for the precise equipment being assigned to sodium ion monitoring. With this combination of equipment the sodium could be calibrated numerous ways. The method most often used was the simple one of using precisely weighed NaCl solutions converted to true normality of sodium ion with density values from the literature (64) for calibration standards, and a meter-recorder combination to record the true mv signal of the sodium and calomel electrodes. The signal is actually equivalent to pNa; thus the potential is a logarithmic function of concentration as demonstrated in the calibration plot of Figure 16. The output could also be converted directly to a linear plot by use of the logarithmic slidewire on the Beckman recorder, but this combination was only reliable down to 0.02 N, because of a voltage mismatch, as shown in Figure 17. With the proper combination of bridge and recorder the output could be plotted linearly in normality units.

The chloride ion concentration was monitored by an Orion 94-17 (solid state) chloride ion electrode. The basic principle is the same as the glass electrode but the potential is developed across a silver, silver chloride membrane (the "solid state" membrane) instead of an ion-specific glass as in the case of sodium ion and pH electrodes. It was used and calibrated identical to the sodium electrode with the other channel of the custom-made pH adapter bridge. The chloride calibrations were similar to Figure 16 with slope of opposite sign, i.e. the mv potentials were positive. The logarithm of chloride concentrations is linear also over the range 0.001—0.1 N but the chloride measurements were not as reliable as the sodium because of the lack of a good double junction calomel reference electrode. An ordinary calomel electrode

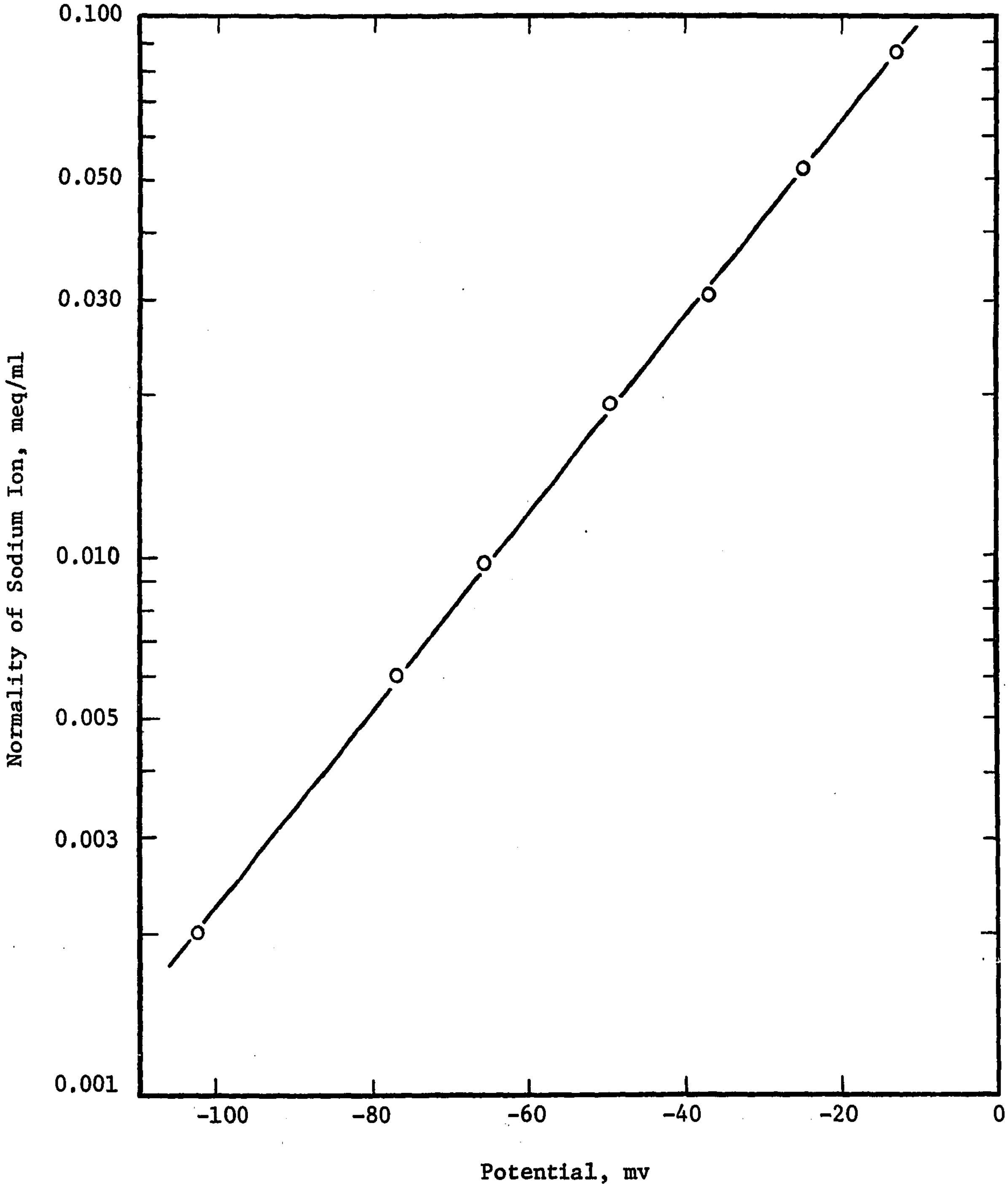


Figure 16. Sodium Calibration of 1/23/68. Corning sodium ion electrode with fiber tip calomel reference electrode and Orion 801 digital meter, calibrated with weighed NaCl solutions prepared 1/22/68.

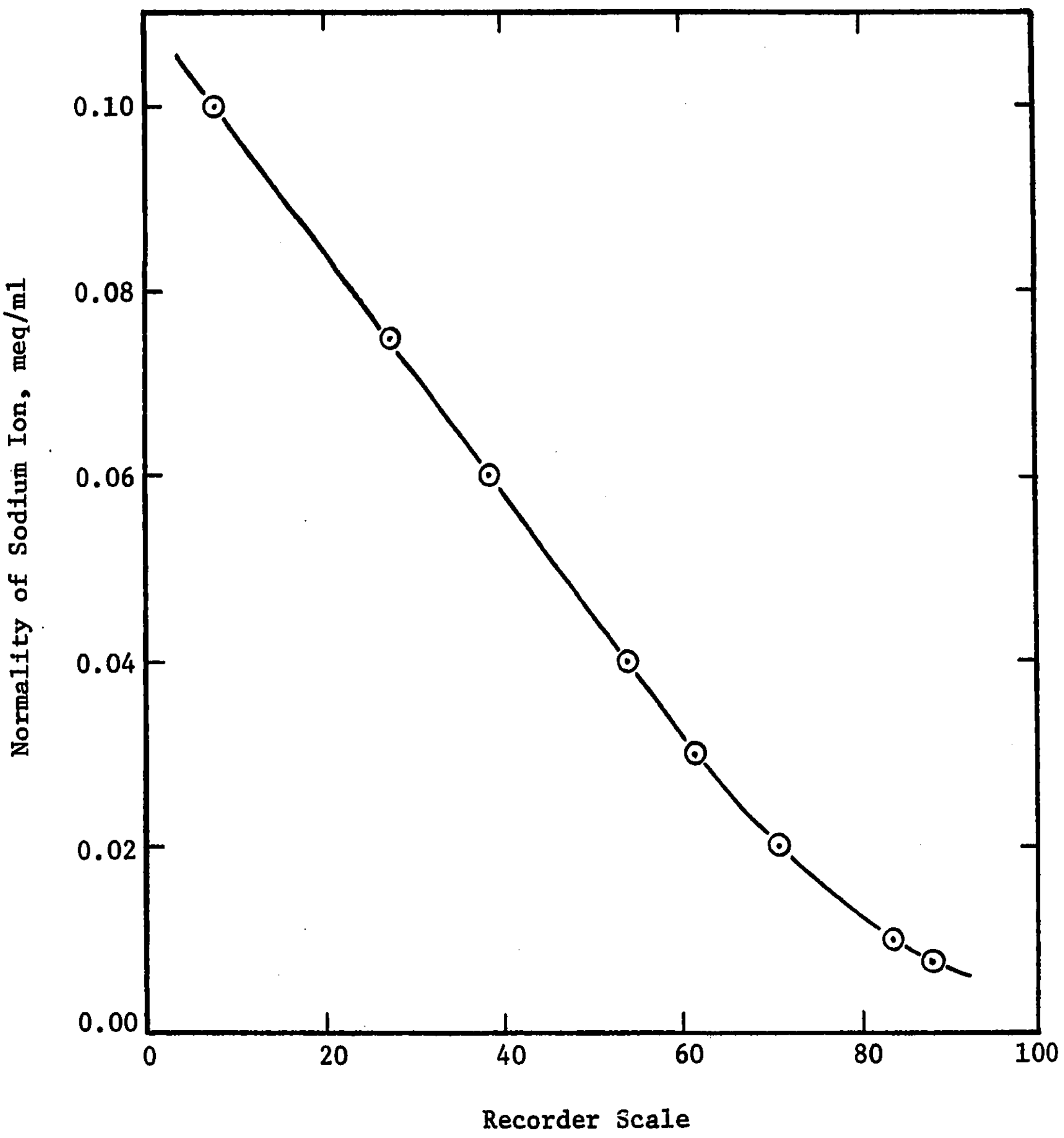


Figure 17. Sodium Calibration of 5/3/68. Corning sodium ion electrode with Orion 801 meter calibrated with weighed NaCl solutions; output voltage converted to linear scale with logarithmic recorder slidewire.

contaminates the solutions with extra chloride ion from its saturated KCl filling solution. One double junction calomel with 0.2 M NH_4OH in the outer contact area was used occasionally but it was physically unsuitable.

It is to be pointed out that for each demineralization-regeneration run that all three of the ion systems were freshly calibrated. A further point is that the sodium system was the most trustworthy of the three. The sodium calibrations changed only minute amounts from day to day, often so small as to be indiscernible.

Voltage controlling and current measuring. All of the demineralization experiments were run at constant potential, usually 600 mv. The voltage across the cell was maintained by a feedback loop ("error sensing") that was separate from the power loop, and usually remained steady within ±1 mv. Switching back and forth from demineralization to regeneration was reliable also within this same ±1 mv. Kepco solid state, Model ABC 2-1M, regulated voltage supplies set up as in Figure 18 were used as the power sources. The Orion 801 meter was more stable and reliable than the usual voltmeter so the potentials were set and checked with it after the proper calibration with a standard cell and potentiometer.

A one ohm, 1% precision, wirewound resistor in the power lead to the carbon electrode served as the probe for the current measurements. Construction of a custom-made voltmeter with a feedback loop involving a solid state operational amplifier allowed the current passing through the one ohm resistor to be measured without using any of that current to drive the meter. Thus the resistance for the power supply was

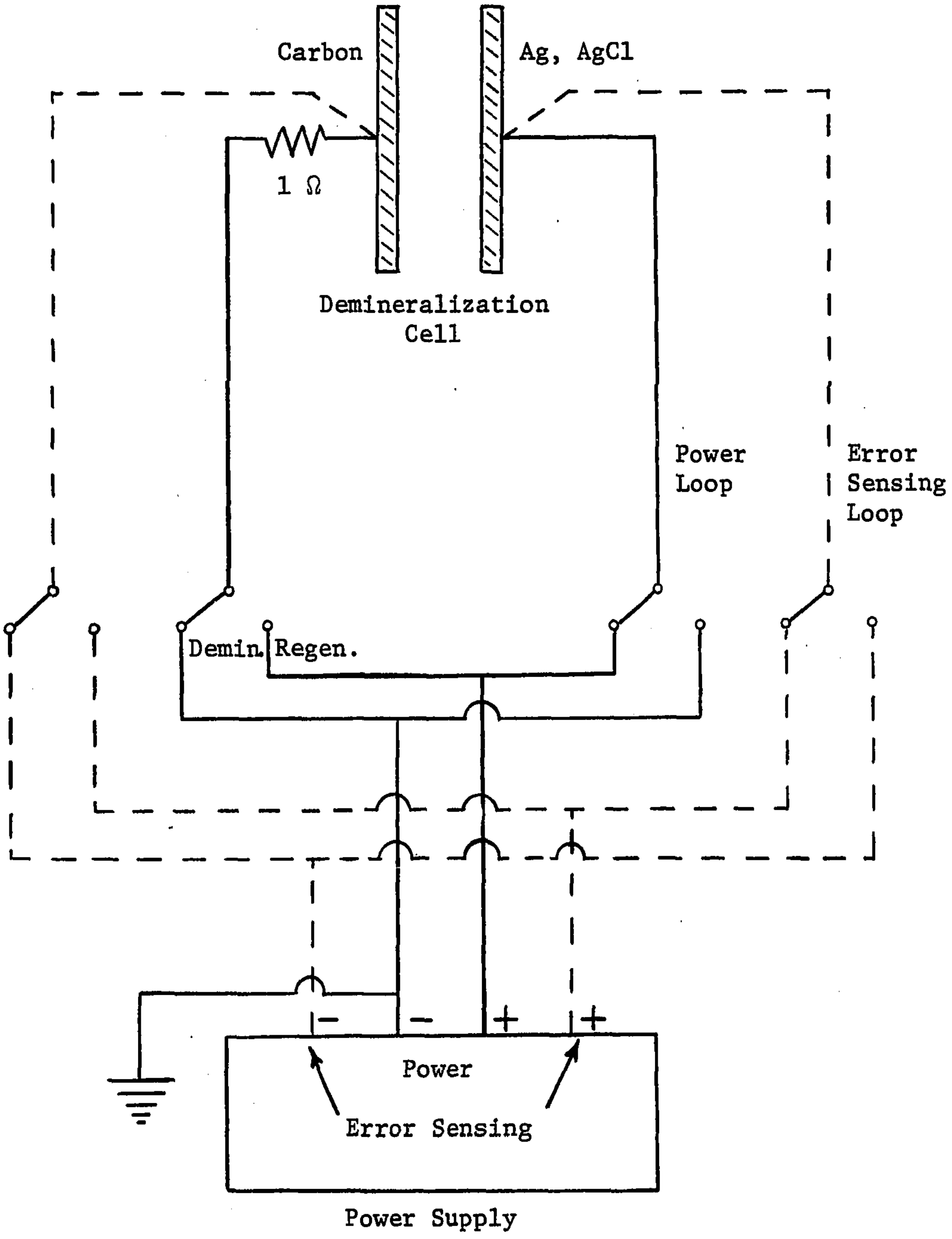


Figure 18. Schematic of Electrical Power for the Demineralization Cell. The contacts are in the demineralization position; for regeneration all four switches are thrown simultaneously. The voltage is determined at the cell with the error sensing circuit and thus maintained at the preset value. The extra one ohm resistor in the lead to the carbon electrode is used in current measurements.

constant and the voltage not disturbed while the milliammeter (voltmeter and 1Ω resistor) required none of the current it was monitoring and consequently gave precise results. Since the current through the cell never reached zero under some experimental conditions the milliammeter was built with variable ranges of 1000, 100, 10, and 1 ma so that the current was measured within ±1-2% over all ranges.

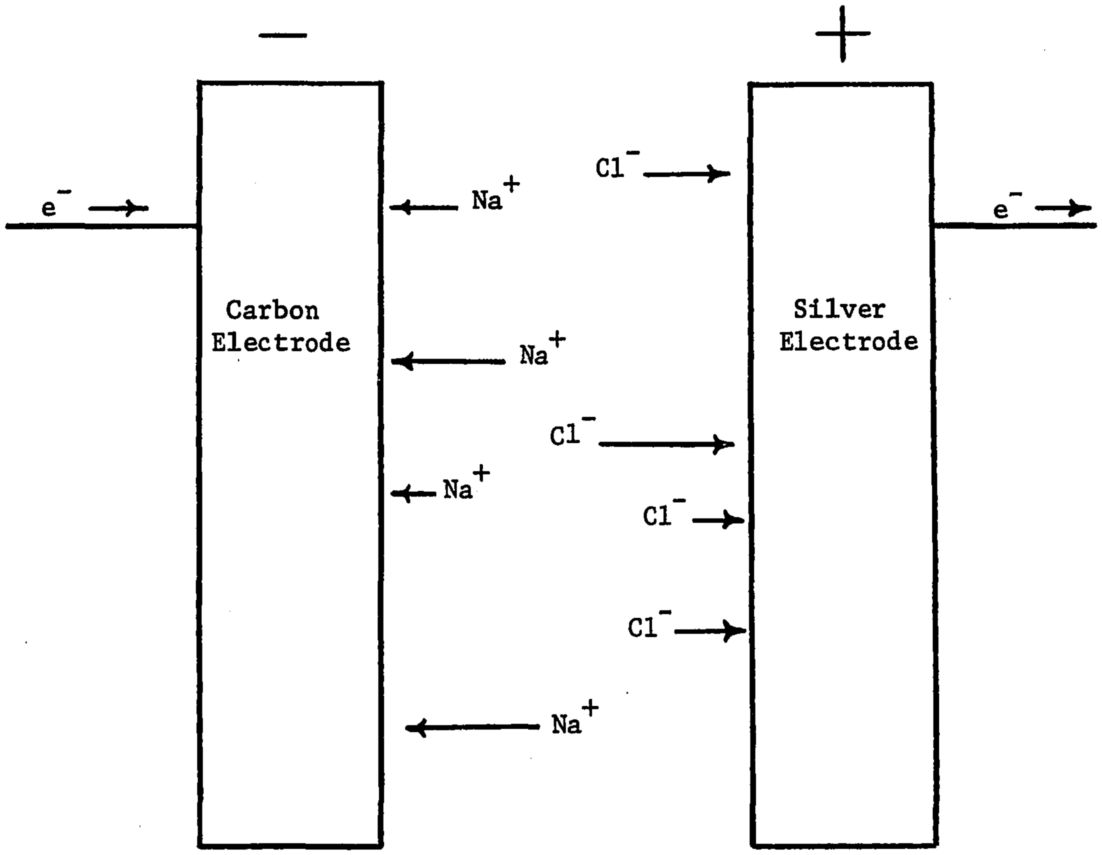
Thus, with all of the above, the flow rate, temperature, feedstream, and potential were maintained at desired constant levels (the parameters) and the sodium ion, chloride ion, and pH of the effluent were measured continuously and simultaneously with the current passing through the cell.

Salt Removal during Demineralization

The electrochemical demineralization of saline water with cation-responsive carbon electrodes has been accomplished with the previously described cell operated at a low, constant potential difference. For the demineralization phase the carbon was reduced, i.e. made negative with respect to the silver, silver chloride, and the silver, silver chloride oxidized. The salt was removed in a general sense as shown in Figure 19.

The silver, silver chloride reaction is well established and it was chosen as the ideal anion-responsive electrode because of this and the fact that it has almost unlimited capacity for chloride ion uptake as well as being non polarizable. Thus the reaction at the silver, silver chloride electrode during demineralization is:

$$Cl^- + Ag \rightarrow AgCl + e^- \tag{2}$$



$$e^- + \rangle C\text{-}(O) + Na^+ \longrightarrow \rangle C\text{-}(O)Na \qquad Cl^- + Ag \longrightarrow AgCl + e^-$$

Figure 19. A General Representation of Salt Removal within the Demineralization Cell during the Demineralization Phase. Reduction takes place at the carbon electrode, which is cation-responsive because of the surface oxides (functional groups) imparted to it during activation with the mixed-acid treatment, and oxidization occurs at the silver, silver chloride electrode. Regeneration is the reversal of the above.

and the overall reaction at the carbon electrode is:

$$e^{-} + {>}\mathrm{C}-(\mathrm{O}) + \mathrm{Na}^{+} \rightarrow {>}\mathrm{C}-(\mathrm{O})\mathrm{Na} \qquad (3)$$

where ${>}\mathrm{C}-(\mathrm{O})$ represents some reactive surface oxide on the carbon. This latter reaction is the summary of many reactions which can occur by different paths, depending upon the potential, reducible species present, and the nature of the surface oxide.

Regeneration of the adsorbed salt to the flowing effluent stream is done by simply reversing the polarity across the cell and thus reversing the reactions in Equations 2 and 3.

With the carbon surface having only a limited number of functional oxides the carbon electrode can only remove an amount of sodium ions which does not exceed this number of oxides, i.e. the carbon electrode has a finite capacity. Thus, the reason for choosing an anion-responsive electrode (silver, silver chloride) with an "infinite" capacity--all measured capacities of the complete cell are due to the carbon electrode's limit.

Plots of the effluent sodium, chloride, pH and the current passed, for a cell operated at 595 mv are shown in Figure 20. The sodium concentration decreases rapidly at first upon switching polarity from the previous regeneration. The removal rate is slowed because of the inaccessibility of more surface groups after the initial reactions with the exposed groups. The rate of replenishing more sodium ions to the cell (flow rate of the influent) begins to overcome the removal rate and the concentration reaches a minimum and slowly returns to the feedstream value. The difference between the feedstream value and the actual

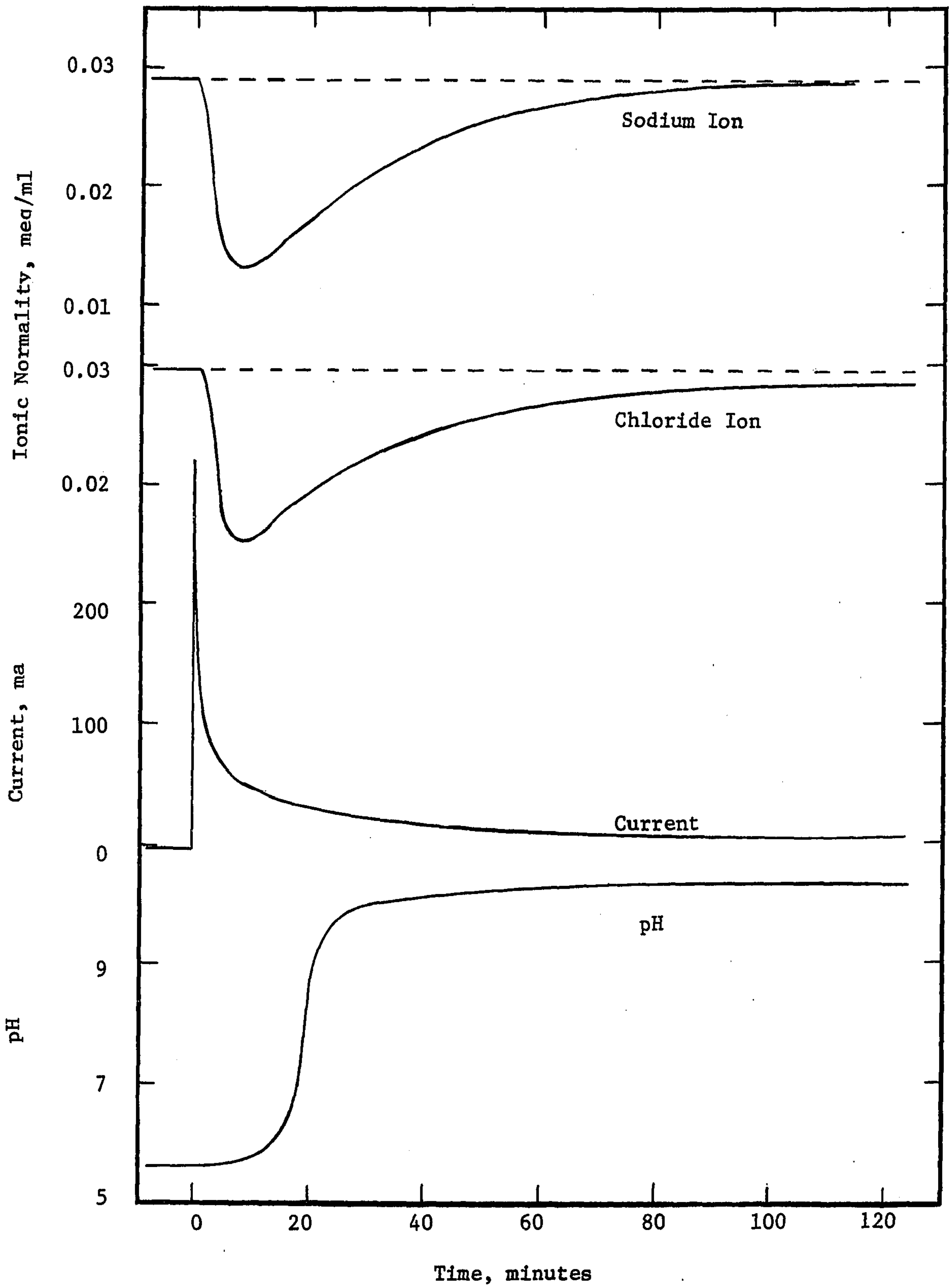


Figure 20. Effluent Concentrations and Current Passed Through a Cell Containing N:G (2:1) MA and Ag, AgCl Electrodes with 595 mv Imposed Across the Cell amd a Nitrogen-Saturated Influent of 0.0295N Sodium Chloride.

concentration is the amount removed from the constant feedstream. The sodium concentration actually returns to the feedstream value because the cation-responsive electrode (N:G (2:1) MA) has a definite limit as to the amount that can be removed.

The effluent chloride concentration follows the same pattern as the sodium, not because of limits the silver, silver chloride possesses but because of the limited capacity of the carbon electrode coupled with the current passed through the cell. The silver, silver chloride will be continuously oxidized and remove chloride ions from solution so long as there is a reduction reaction, beyond the proper potential interval, occurring within the cell.

Over most of the time that salt is removed the current reflects the sodium concentration pattern. The first part involves a great deal of current during the early rapid removal of sodium and changes slope as the rate of salt removal is slowed. The current does not actually reach a zero value, either on demineralization or regeneration, but goes to low values such as 0.3—0.8 ma. A look at the effluent pH explains the small current level still maintained within the cell. Another reduction reaction beyond sodium removal is still occurring within the cell: an equivalent number of hydroxide ions are being produced by the excess current beyond sodium removal. The mass balance is maintained by the subsequent removal of an equivalent amount of chloride ions for the oxidation step; thus the chloride current, and pH never return all the way to the feedstream values.

pH Changes in the Effluent

The effluent pH from cells containing a carbon and a silver, silver chloride wire mesh electrode rises above neutrality during the demineralization phase of the cycle. Upon switching to the regeneration phase the pH immediately falls below neutrality.

The effluent from a cell with 600 mv imposed across it and 0.030 N NaCl solution flowing at the rate of 50 ml/hr through it rises to a maximum pH of approximately 10.8 immediately after salt removal and drops slowly over the next few days. The slow drop in pH is so gradual that the level appears to be constant, until it has been checked for many days.

Upon saturation of the feedstream with oxygen at atmospheric pressure the pH rises even higher. In Figure 21 it can be seen that the pH reaches a value of 11.3. Even after six days the pH is still quite high, about 10.7.

The implied effect is even more pronounced when elaborate precautions are used to eliminate oxygen. A complete cell, along with its pump, pH electrodes, and conductivity electrodes, was enclosed in an atmosphere box swept with nitrogen (these experiments were done before the acquisition of the specific-ion electrode system). The reservoir was freed of oxygen by bubbling with pyrogallol-scrubbed nitrogen and connection was made to the cell with continuous glass tubing. The resulting low rate of hydroxide production can also be seen in Figure 21. Even with mechanical difficulties the production of hydroxide did not exceed 0.08 meq for the entire twelve days. This was the situation when the feed pH was 6.7—6.8 and the flow rate was 50 ml/hr. This compares with 3.1 meq of hydroxide produced in ten days when the influent solution was open to the air. Hydroxide production never exceeded 5×10^{-4}

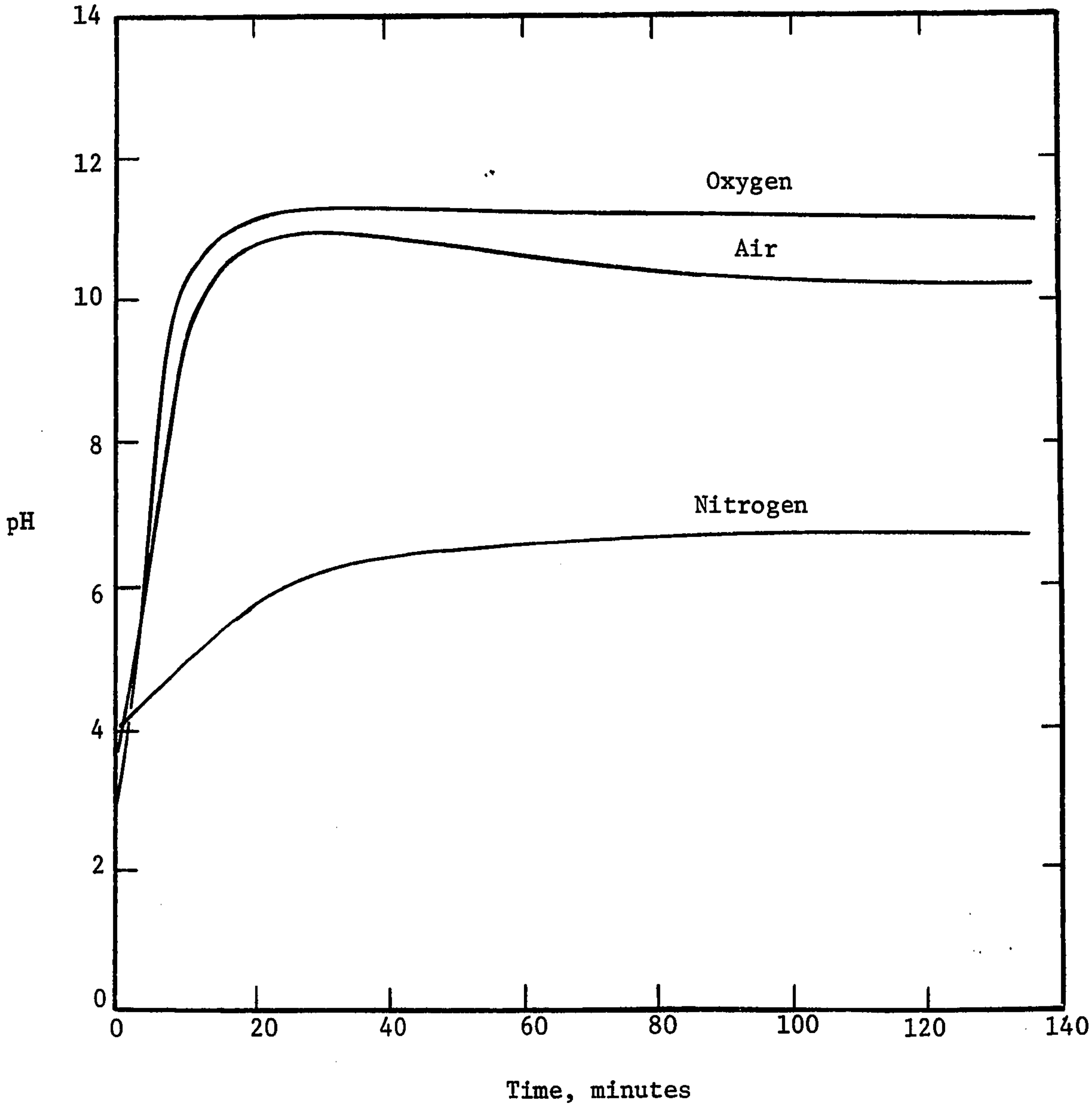


Figure 21. Effluent pH of Demineralization Cells with various Saturating Atmospheres. The effluent pH during the actual salt removal period with the feedstream solution saturated with the indicated gases. The nitrogen-saturated case is at a lower flow rate than the others. The nitrogen-saturated effluent pH rose to higher values after salt removal as is shown in Figure 20 for a cell under similar conditions at a higher flow rate.

meq/hr in this nitrogen experiment. As can be seen in Figure 22, the pH indicates no excess hydroxide was produced during actual salt removal, because the low rate of hydroxide production in the nitrogen situation is the limiting rate in salt removal, i.e. the pH was at neutrality during the ion exchanging and rose above seven only after no more sodium ion was removed from solution.

The voltage imposed across the cell determines the rate of hydroxide production. A cell identical with the ones used in the earlier experiments with oxygen-saturated feedstreams was operated at 565 mv instead of the usual 600 mv across it. The effluent pH was lower for the lower voltages. Of course, the voltage also determines the reaction which occurs. In the constant current experiments at Rocketdyne Corporation (65, 67) on mixed-acid treated carbon electrodes essentially identical to N:G (2:1) MA the influence of O_2 upon pH was not noticed. In demineralization experiments at constant 0.5 and 1.0 ma the voltage did not rise to a level comparable with the present experiments and the reaction with oxygen did not occur, even though the solutions were open to the air. The pH changes were only measured at the electrode with pH paper but they were of the same approximate order of magnitudes as the present nitrogen experiments on N:G (2:1) MA.

The production of hydroxide during the demineralization phase involves a reduction reaction, most likely with water, and it could be explained by the following possibilities:

$$e^- + H_2O \rightleftarrows \tfrac{1}{2}H_2 + OH^- \qquad (4)$$

$$2e^- + H_2O + \tfrac{1}{2}O_2 \rightleftarrows 2OH^- \qquad (5)$$

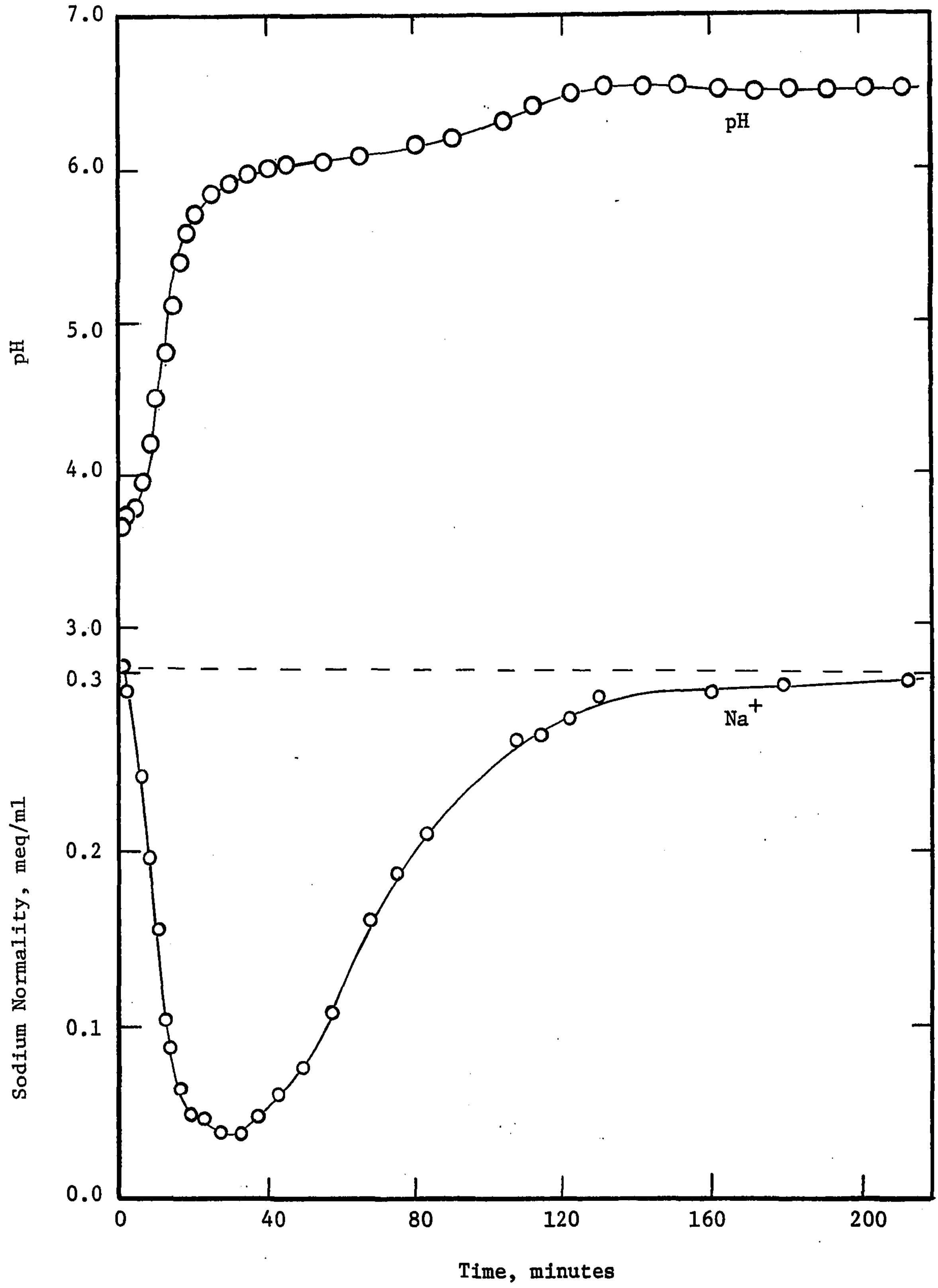


Figure 22. The Effluent pH and Na$^+$ from a Cell Enclosed in a Nitrogen Atmosphere Box. The pH later rose to a high point of 8.6 at 70 hours. Samples of the effluent were withdrawn and measured on a flame photometer and with a pH glass electrode.

$$e^{-} + H_2O + R \rightleftarrows RH + OH^{-} \qquad (6)$$

where R in Equation 6 is a reducible surface group on the carbon, such as carbonyl. Each of the above reactions could then be involved in an acid-base ion-exchange step for the removal of sodium ions from the solution, with the high pH being the driving force.

$$R\text{—}COOH + OH^{-} + Na^{+} \rightarrow R\text{—}COONa + H_2O \qquad (7)$$

The last reduction reaction, Equation 6, has a finite limit: the number of R groups on the carbon. Thus if this reaction is responsible for hydroxide generation, then the number of R groups should be equal to, or less than, the demineralization capacity for sodium plus the excess hydroxide lost to the effluent stream. (The number of R's would be less than this sum for the case of other groups being operational under these conditions.) In fact, for the hydroxide even to be in the effluent means that some of the R groups are in the form RH, an unlikely situation with the high pH often found in the cell, <u>unless</u> the group RH has a high pKa. Furthermore, the presence of a reducible species such as O_2 should have no influence upon the generation of hydroxide if Equation 6 were the major reaction, and it is obvious that oxygen has a very great influence upon the production of hydroxide. Therefore it would seem that in the presence of oxygen that Equation 5 is the major reaction and that the other two are only of minor importance or non-existent under these conditions.

The reaction in Equation 4 has been proposed by the group at Rocketdyne Corporation as the main step in the removal of salts by electrochemical demineralization with carbon electrodes (65, 67). The presence of the reduced product species, either as adsorbed atomic hydrogen or as gaseous hydrogen is difficult to prove below gassing potentials, above which bubbles are produced.

It is conceivable that all three reactions are operating in the demineralization cell under various conditions. Equation 5 is obviously occurring anytime that oxygen is present. The simple reduction of water by the reaction in Equation 4 is not so obvious and in the oxygen-free case the reaction is not definitely known.

The pH does rise slightly in the oxygen-free situation, but the amount of excess hydroxide produced is small when compared to the amounts produced in the presence of oxygen, as stated previously. That the pH does change and does rise above the neutral influent in the oxygen-free situation is evidence for the production of hydroxide. The effluent pH in Figure 20 is also from a cell with nitrogen-saturated feedstream and it rises to a level slightly above 10 after being at 5.6 after regeneration, an even greater pH change than the previous oxygen-free experiment.

The effluent from all experiments with nitrogen-saturated feedstreams became acidic upon regeneration. This acidity could be explained by the oxidation of the adsorbed hydrogen, which was generated during the reduction of water without the presence of oxygen as in Equation 4, no matter what the form of the hydrogen, i.e. whether it is atomic or molecular (65):

$$H_{ads} \rightarrow H^+ + e^- \qquad (8)$$

Tha acid could also be due to the oxidation of water, as in the following equation:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (9)$$

and the oxygen would be adsorbed and thus be available for subsequent hydroxide production during the demineralization phase as in Equation 5.

Either set of reactions, i.e. Equations 5 and 9 or Equations 4 and 8, would be consistent with the observed pH changes with demineralization-regeneration by ion-exchange with acidic surface oxides.

Equation 6 coupled with ion-exchange reactions could also account for the observed pH changes without any dissolved gases entering into the reactions. The role of the groups R and RH would thus be indirectly connected with sodium ion removal. The regeneration of the reduced group would be:

$$RH \rightarrow R + H^+ + e^- \qquad (10)$$

and R would never be associated directly with sodium ions. <u>If</u> the groups RH had pKa's low enough so that they behaved as ion-exchangers and took up sodium ions then hydronium ions would not be generated during regeneration, for the groups would be RNa instead of RH. Both sodium and hydronium ions <u>could</u> be regenerated if some of the groups RH have pKa's above and some below the pH of the solution, e.g. there might be more than one type of RH, say carbonyl-hydroxyl and aldehyde groups. Thus, Equation 6 could only be involved if the pKa's of the reducible groups R are high.

The generation of excess hydroxide in the oxygen-free case was usually low, often less than 0.2 meq during 24 hours after salt removal for flow rates of 110-120 ml/hr. The pH drops slowly for days and an accurate evaluation of the total excess hydroxide is impossible to obtain, but it appears to be 0.3—0.4 meq per gram of carbon.

Ion-Exchange with High pH Solutions

The cation-removal capacity of the demineralization cell with carbon and silver, silver chloride electrodes is determined by two types of reactions. One is reduction, as explained in the previous section. The other is ion-exchange with acidic surface groups (carboxyl and phenolic hydroxyl) in the presence of high pH solutions. The latter is the result of the electrochemical reduction involving water, as shown in previous sections.

If the majority of the demineralization capacity of the carbon electrodes is due to ion-exchange and not to a primary electrochemical step involving reducible surface groups, then demineralization should occur with high pH solutions, no matter what the source. The titration with sodium hydroxide and ethoxide indicate capacities approaching 2.1—2.2 meq/g with all of the acidic groups. This is more than sufficient to account for the demineralization capacities of the electrochemical cells, which are usually 0.9—1.2 meq/g. To further clarify the capacity of N:G (2:1) MA for sodium ions extra titrations were done with NaOH-NaCl solutions. Because of the low concentrations and the lack of reliable equipment the values determined lack good precision. The sodium concentration determinations were done with a Coleman falme photometer and were the major source of errors. The results are presented in Figure 23 as the amount of sodium ion uptake at equilibrium concentration of both sodium ion and hydroxide.

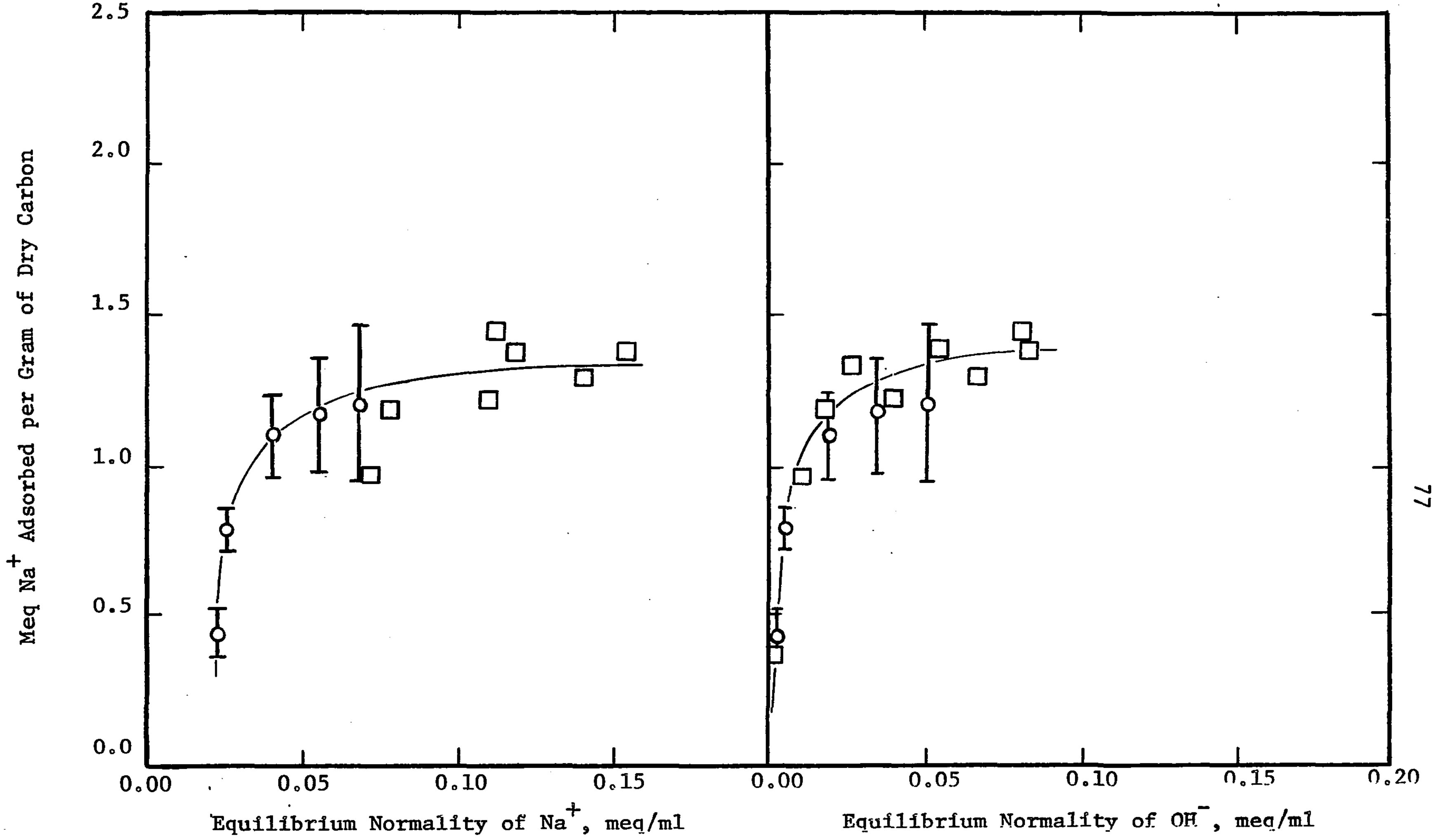


Figure 23. Ion-Exchange Capacity of N:G (2:1) MA Determined by Titration with NaOH–NaCl Solutions. The data lack good precision and are therefore used as an indication of the ion-exchange capacity only.

From the relative size of the previously determined capacities it is logical that a demineralization cell without applied potential should thus show sodium ion uptake upon introduction of NaOH-NaCl solutions. The cell would remove sodium up to a level consistent with the pH of the solution only, whereupon the process would stop and the effluent would be identical with the feedstream. Upon application of an applied potential at this point the pH of a nitrogen-saturated stream would not change and any demineralization which occurred would be due to the primary reduction of redox groups on the carbon. Any changes in the pH would indicate the reduction of water and the additional demineralization capacity would be simply due to additional ion-exchange at the new pH.

Experiments were conducted with NaOH-NaCl solutions flowing through a demineralization cell. The procedure consisted of 1) a conditioning period, 2) measuring of an ordinary demineralization-regeneration cycle, 3) electrical discharging of the cell, 4) introduction of a high pH feedstream with no applied potential, and finally 5) the reapplying of a potential for further demineralization-regeneration. It would have been desirable to use the cell for further experiments beyond this point, however, the use of a high pH feedstream suspends the carbon and creates salts of humic acid (66). After a few hours the effluent became coffee-colored; thus ending the life of the electrode.

The discharging of the cell took several days (see later section on potential decay) and was done with sodium chloride solution flowing through the cell. When the cell voltage approached a constant level the feedstream was altered to a mixture of nitrogen-saturated NaOH-NaCl with a pH of 12; thus resulting in the expected demineralization as shown in

Figure 24. The run was allowed to continue for a few hours until the effluent sodium concentration returned to the feedstream value. A voltage of 600 mv, with the polarity of an ordinary demineralization run, was then imposed across the cell and further demineralization occurred.

The ion-exchange capacity of this cell with the hydroxide as the driving force was 0.96 ±0.06 meq Na^+/g. The additional demineralization upon application of 600 mv was very small, being about 0.030 ±0.002 meq Na^+/g. Using the latter as an indication of demineralization by the primary electrochemical reduction of surface groups gives an estimate of less than 3% of all reactive oxides for such reducible oxides as carbonyl or ether. The effluent pH did change slightly upon application of the potential, with no oxygen present, which can be explained as being due to direct reduction of water as in the following manner:

$$e^- + H_2O \rightleftarrows \tfrac{1}{2}H_2 + OH^- \qquad (11)$$

in which case the additional sodium ion uptake would be simply due to ion-exchange at a higher pH. The pH change was so small as to be unreliable, so it is not clear which process took place during the additional demineralization.

Sodium Chloride Adsorption

It has been known for some time that carbons adsorb ions from neutral salt solutions with no outside driving force. An earlier literature survey (61) revealed that NaCl is adsorbed to a level of only 0.05—0.10 meq/g carbon at equilibrium concentrations comparable to Figure 23, i.e. 0.1—0.2 N, on most activated carbons.

There was considerable question in the literature about the

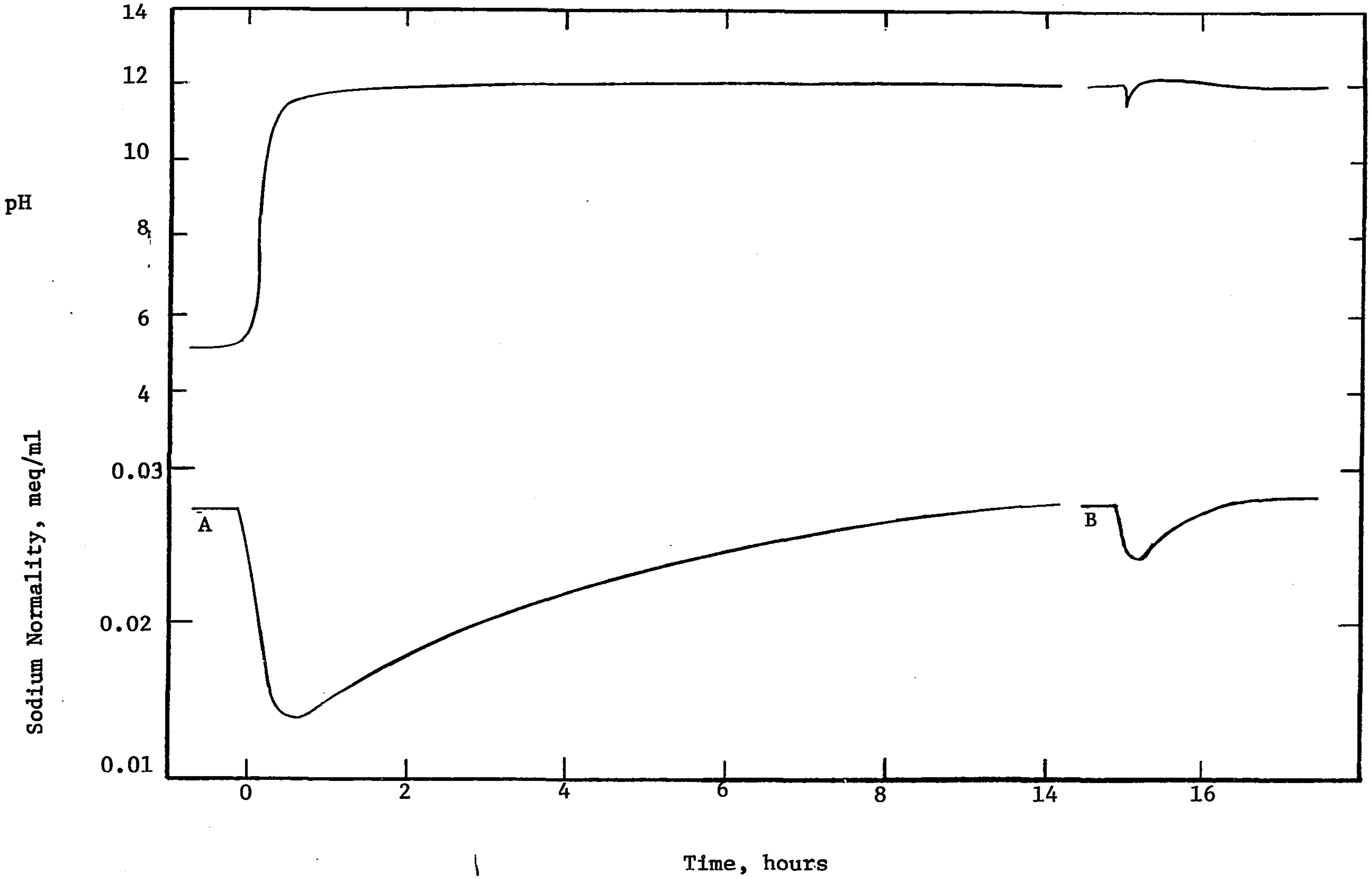


Figure 24. Demineralization with High pH Feedstream. At point A, the NaOH-NaCl solution was introduced to the cell with no applied potential. At point B, 600mv was imposed across the cell, which still contained nitrogen-saturated NaOH-NaCl.

mechanism of removal. Carbons possess some anion-responsive groups, usually in small numbers, from ordinary activations. Of considerable importance is the question of whether hydrolytic adsorption occurs or not, i.e. does the pH change for sodium chloride adsorption from neutral solutions? From the present experiments it would seem that pH changes may have occurred in earlier investigations and that the solutions were not adequately checked for all ions. Thus some of the reported values are not for salt adsorption but rather for the particular ion measured. This was pointed out earlier (61) and, as a result, some work was done at Oklahoma Baptist University to determine NaCl adsorption from neutral solutions (60). Investigations on untreated Norit A charcoal revealed the expected pH changes in the acid direction. As also expected the charcoal had higher capacities for cations than anions. At equilibrium sodium concentrations approximately equal to the feedstream values used in demineralization studies, the sodium ion uptake was 0.15—0.20 meq/g of carbon.

Similar investigations were conducted on mixed-acid treated Norit at Rocketdyne Corporation where the reversible ion-exchange capacities were determined. The carbon was placed in neutral sodium chloride solutions for five days and then removed, washed, and dried. The sodium chloride was regenerated in hydrochloric acid solutions and the sodium measured. The amount of sodium removed and then regenerated was 0.28 ±0.02 meq/g from solutions of original concentrations equal to the feedstream concentrations of the present demineralization experiments. A comparison value from their investigations is not readily available since the equilibrium concentrations are not reported, but it should be slightly higher than 0.28 meq Na^+/g (67).

Determinations of total capacity for sodium on identical carbons as those used on this project, i.e. N:G (2:1) MA, were reported as 2.2—2.5 meq/g, which compares very well with the approached limit of the present hydroxide-ethoxide titrations. Values were also reported for the individual carbons. Mixed-acid treated Air-Spun graphite has an approximate capacity of 0.45 meq Na^+/g, determined from electrode capacity, and mixed-acid treated Norit A charcoal had a capacity of 3.0 ±0.5 meq Na^+/g, determined from NaOH exchange capacities. Based upon the latter values, one gram of N:G (2:1) MA would have a capacity for sodium of 2.3 ±0.2 meq/g (65).

Thus the majority of the ion-exchange capacity of the activated carbon in the present studies is due to the mixed-acid treated Norit A, as is to be expected from the earlier discussions of graphite and activated charcoals. The presence of the graphite hinders the adsorption of sodium by a dilution effect due to its lower capacity. This disadvantage is offset by the physical stability and low resistance imparted to the electrodes by the presence of the graphite.

Open Circuit Potential Decay

Allowing the potential of a demineralization cell to decay after normal operation again points to the great influence of oxygen upon the electrode reactions. Earlier open circuit studies of cells with N:G (2:1) MA and Ag, AgCl electrodes and air-saturated solutions flowing through the cells approached an equilibrium potential of +174 mv, carbon positive with respect to silver, silver chloride (61). Present studies without the presence of oxygen approached a value of 40 ±10 mv. The results of both experiments are presented in Figure 25.

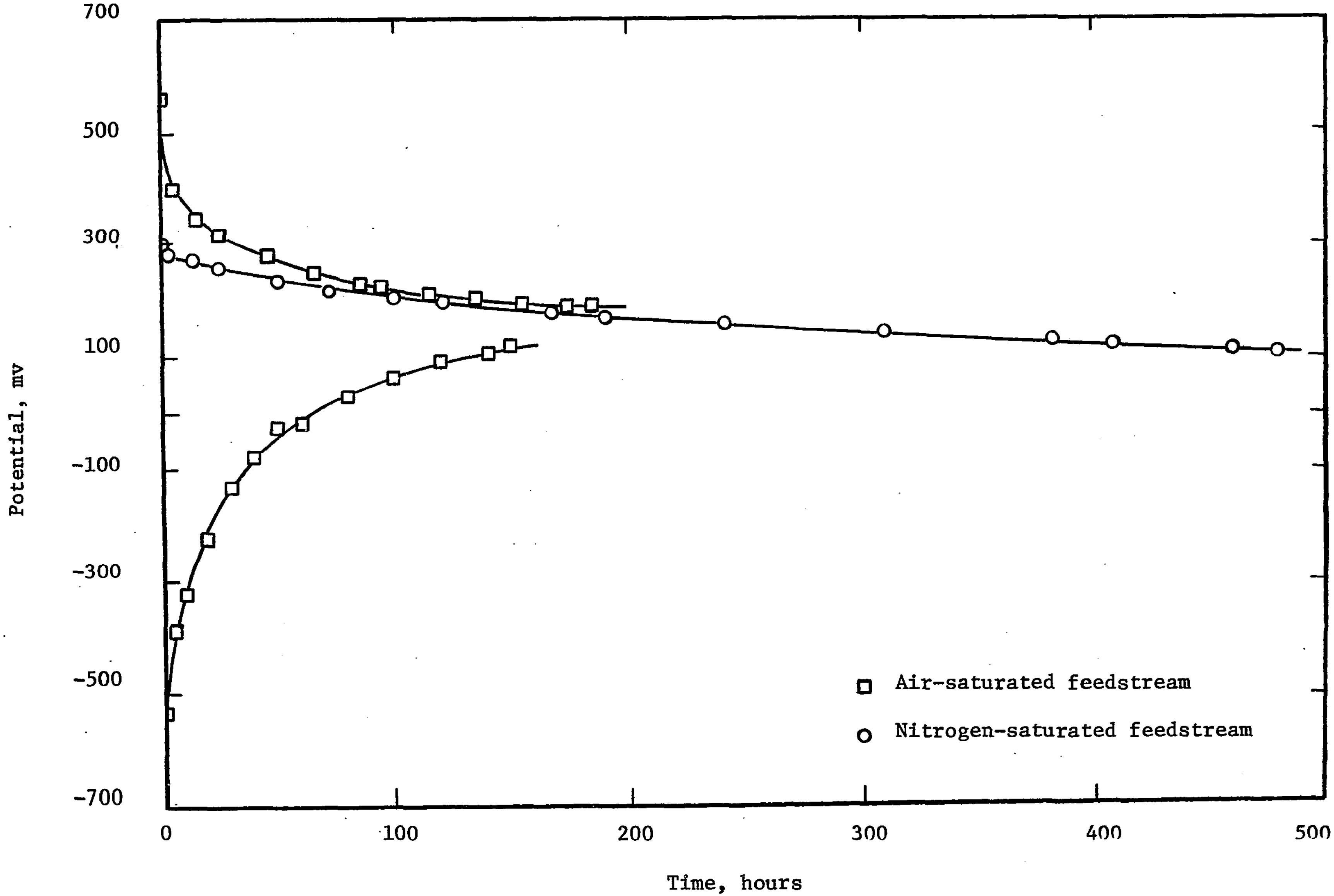


Figure 25. Open Circuit Potential Decay of Demineralization Cells. Potential decay of cells containing carbon [N:G (2:1) MA] and Ag, AgCl electrodes after removal of applied potential. The upper curves are after regeneration; the lower one is after demineralization.

The air-saturated experiments were started after regeneration at 553 mv (upper curve) and demineralization at 562 mv (lower curve). The same cell was used for both runs after completing many demineralization-regeneration cycles before and between the two experiments. The experiment with nitrogen-saturated feedstream had also been cycled many times and the applied voltage was removed after regeneration at 300 mv and the cell allowed to discharge across a high impedance potentiometric recorder, the same as in the air-saturated case. The potential decay is quite slow and in the nitrogen situation was still changing at a very low rate even after two months.

The presence of oxygen is even more dramatically shown in Figure 26. The cell with the nitrogen-saturated feedstream was accidently exposed to air on the 47th day and the potential immediately rose. The situation was corrected after three days with the exclusion of oxygen and the voltage returned to the previous lower value. It is obvious that an oxygen potential is sometimes involved, but it is not known what the reactions are.

One of the earlier postulations of the demineralization studies concerned the ability to regenerate adsorbed salt by simply removing the applied potential. This was attempted and no measurable increase of salt in the effluent could be detected. Evans and Hamilton (65) also detected no sodium ion release after allowing N:G (2:1) MA and Ag, AgCl electrodes to stand under open circuit conditions for several hours.

It would appear from Figures 25 and 26 that the cell does actually regenerate some of the adsorbed salt to the flowing effluent but only at a very slow rate, so slow as to be undetectable with ordinary measure-

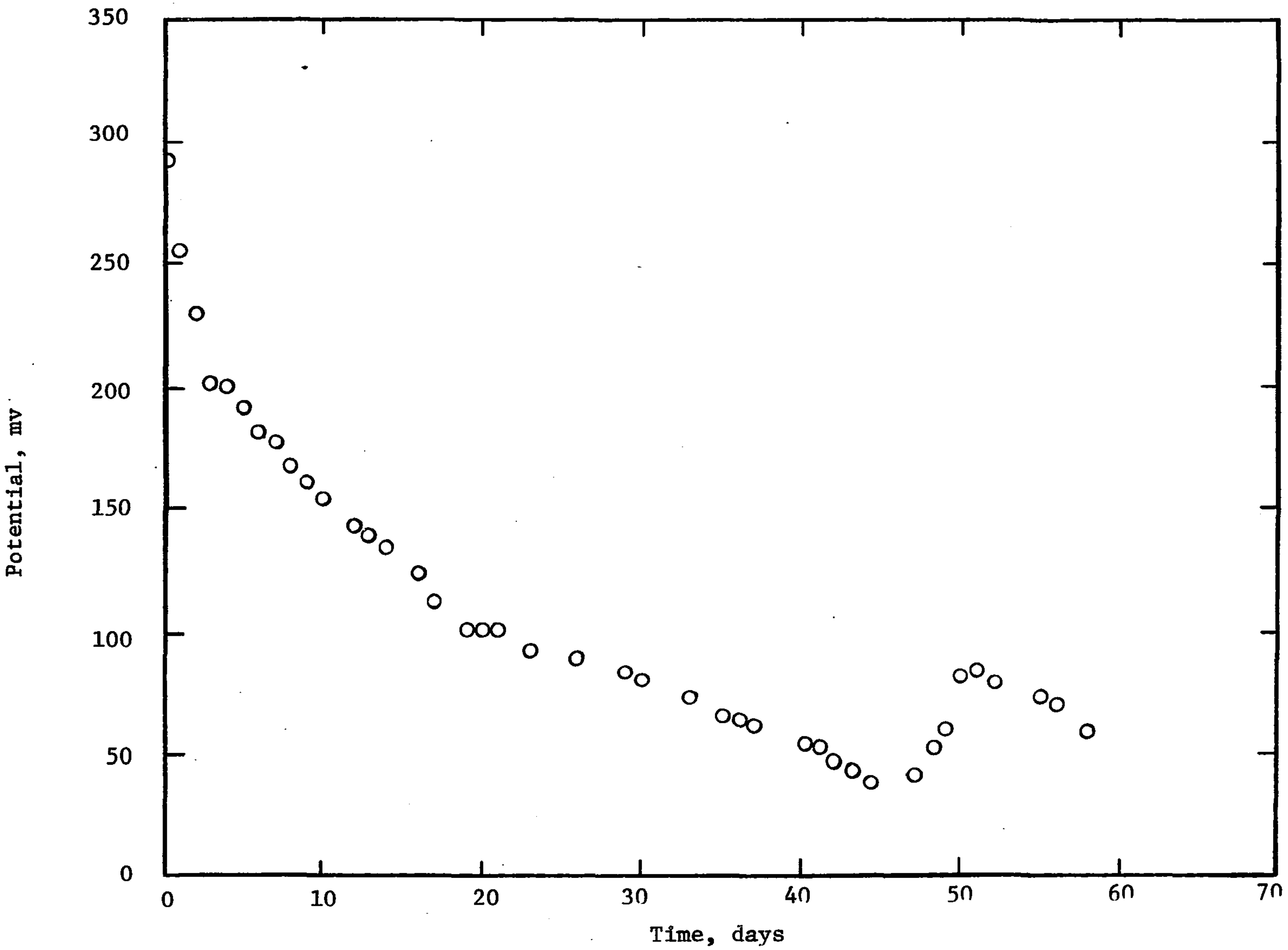


Figure 26. Potential Decay of Demineralization Cell after Regeneration at 300 mv. Open circuit voltage drop of a cell containging N:G (2:1) MA and Ag, AgCl electrodes with nitrogen-saturated feedstream flowing through the cell. Air was accidently introduced to the system on the 47th day, resulting in a temporary voltage rise, which was corrected by exclusion of air three days later.

ments. The equilibrium potential, with or without the presence of oxygen, is in the regeneration direction (carbon positive with respect to the silver, silver chloride electrode) and should therefore result in regeneration.

The cell under open circuit conditions is not actually at equilibrium when a constant potential is reached, but rather is at a steady state because of the flowing NaCl solutions. This being at steady state may result in reactions with dissolved gases, such as the migration of adsorbed hydrogen from the carbon to the silver, silver chloride electrode to reduce silver and alter the pH.

$$\tfrac{1}{2}H_2 + AgCl \rightarrow Ag + H^+ + Cl^- \qquad (12)$$

A reaction of this type would take place at such a slow rate as to be undetectable.

The open circuit potentials should be used with caution in calculations involving the equilibrium E^o potential because of the steady-state conditions. Calculations of potentials for reactions involved in demineralization-regeneration are not possible because of the unknown IR drop across the cell and the overvoltages due to adsorbed gases in the working cell; thus decisions between possible reactions based upon potential calculations cannot be made.

IV. DISCUSSION AND CONCLUSIONS

Carbonaceous materials were chosen for electrode fabrication in electrochemical demineralization of saline water because of the low cost, availability, and physical properties such as high surface area and low resistance. These desirable properties were further enhanced by the ion selectivity and respectable ion adsorption capacities of the carbons. The latter were improved with activation, usually with concentrated nitric-concentrated sulfuric acids.

Activation with concentrated sulfuric and nitric acids changes the properties of the carbon drastically. The most important change is the imparting of functional oxide groups to the surfaces of the carbon particles. With the vigorous activation from the mixed-acid treatment it is very likely that all possible reactive sites have been converted to a functional oxide, of one form or another. Because the activation is at room temperature in an aqueous environment the majority of the oxides are acidic in nature, mostly carboxyl and phenolic hydroxyl.

The surface oxides are acidic enough to be titrated with basic solutions and this was used to identify and distinguish between the major groups because of the differences in ionization constants of the acidic groups. The total acidity of N:G (2:1) MA, as determined by titrations, is 2.1 ±0.1 meq/g; an amount which is verified by similar evaluations by Evans and Hamilton at Rocketdyne Corporation, also on N:G (2:1) MA (65).

The great majority of the oxides are found to exist as carboxyl groups. Titration with the weak bases, sodium carbonate and bicarbonate, gave values of 1.35 ±0.15 meq/g for the strongest acidic group, carboxyl. That carboxyl exists on the carbon was confirmed from the 1590 and 1380 cm^{-1} bands in the IR spectra of the sodium salts of suspended particles of the carbon, under which condition the group is found as a carboxylate ion.

The ion-exchange determinations with NaOH-NaCl titrations indicated a level of sodium ion adsorption identical with the amount of carboxyl groups, i.e. 1.4 ±0.1 meq Na^+ adsorbed per gram of dry carbon. This same numerical quantity appeared in the studies at Rocketdyne Corporation on N:G (2:1) MA as the point of occurrence of inefficiency in electrode operation. Their carbon electrodes operated efficiently up to a level of 1.20—1.30 meq Na^+/g, even though the carbon possessed a total acidity of 2.3 ±0.2 meq/g. The inefficiency point was noted as a drop in efficient sodium capacity and the beginning of pH changes. The latter value was confirmed with independent electrode studies on the two carbons, both of which exhibited the same behavior. Mixed-acid treated Norit A became inefficient at 1.3—1.7 meq Na^+/g, and mixed-acid treated Air Spun graphite operated efficiently up to 0.45 meq Na^+/g, where the cation capacity changed drastically. The weighted sum of the last two would give a value of 1.2 ±0.2 meq Na^+/g, very close to the actual measurement.

All of these values are within the error of the carboxyl determination with carbonate-bicarbonate titrations. Thus, the carboxyl groups have pKa's sufficiently lower than the other oxides and readily act as the major ion-exchange groups. In order to utilize the next major group, hydroxyl, as ion-exchangers the pH has to be quite high and this situation could only occur within the demineralization cell with reduction of oxygenated water and there is no indication that the pH was high enough even then. The demineralization cell therefore has a limited cation capacity of 1.4 meq/g, except when the pH is allowed to go quite high.

Even this limit of 1.4 meq/g was not utilized entirely, for the pH within the demineralization cells never exceeded 11.3 in normal usage and often reached values only in the ten's. At the latter pH's the ion-exchange capacity as determined by NaOH-NaCl titrations is 0.9—1.2 meq/g. These values are the same as the measured capacities of the demineralization cells. Thus, the measured amount of carboxyl groups, which is, of course, numerically equal to the ion-exchange capacity, is more than sufficient to account for the measured cation capacity.

The predominance of carboxyl is also shown in the amount of CO_2 evolved during thermal decomposition of the surface oxides. From H. P. Boehm's observations it is quite likely that the first two peaks of the DTA pattern of N:G (2:1) MA are due to carboxyl decompositions. The first, small peak at 250°-350°C is most likely a weakly held carboxyl, perhaps of the lactone form, while the second very large peak centered at 500°-510°C is nearly all carboxyl decomposing to CO_2. Boehm *et al.* had noted that the first carboxyl was formed at activation temperatures below 400°C. There is no proof in the present studies that this is in the lactone form or not, but if lactones are present the relative amounts of lactones to free carboxyls would be similar to the relative sizes of the two peaks.

The presence and amounts of phenolic hydroxyl groups place it as the next group of importance after carboxyl. The difference between the hydroxide and carbonate-bicarbonate titrations establish hydroxyl at 0.76 ±0.01 meq/g, almost the entire balance of the detectable surface oxides. It has been associated with the 1150-1155, 1265, and 3430-3440 cm^{-1} bands of the neutralized suspension particles, in which it exists as $>$CONa. A band also appears at 1070 cm^{-1} with neutralization by the weaker base, Na_2CO_3, apparently the COH form of hydroxyl. Decomposition products of hydroxyls are not so well established, so that the DTA product gases cannot be readily separated into those resulting from hydroxyl and the other oxides.

Hydroxyl groups play an indeterminate role in the demineralization reactions but they apparently have such high pKa's that they have no direct role in cation removal. Hydroxyl groups are important in adsorption of polar adsorbates such as water and no doubt furnish sites for catalytic reactions.

The detection and determination of carbonyl groups proved to be a difficult undertaking. Earlier titrations with the different bases showed a small difference between amounts neutralized with sodium carbonate and sodium bicarbonate. Usually the difference was 0.25 ±0.05 meq/g, or approximately 9-14% of the total detectable oxides. This difference was <u>not</u> reproducible. Later titrations yielded the same value for carbonate neutralization as that for bicarbonate; thus, indicating that carbonyl was absent in association with carboxyl as a lactone, etc.

Titration with sodium ethoxide in ethanol solutions should neutralize all acidic groups and form salts of hemiacetals with carbonyl groups; thus any difference between the amount neutralized with ethoxide and that neutralized with hydroxide would indicate how many carbonyl groups are on the carbon surface. Titrations on N:G (2:1) MA yield only 0.1 meq/g for carbonyl, or less than 5% of the total groups. A value of 0.1 meq/g is within the error of the titration method.

Another indication of carbonyl amount was the additional demineralization upon application of 600 mv after demineralizing with oxygen-free NaOH-NaCl solutions and no applied potential. This small amount was only 3% of the total amount removed and it was questionable because the pH changes which occurred made the interpretations unreliable (see Figure 24). If the pH did change to a higher level, then the additional cation capacity was due to additional ion-exchange and not direct electrochemical reduction of a surface group such as carbonyl.

The infrared spectra of the neutralized suspension particles contained a band at 1775 cm^{-1}, which is usually associated with a carbonyl, but the identification of the form of the carbonyl is not possible. Likewise the separation of the evolved gases from the DTA experiments is not possible, since it is not known definitely to what carbonyl decomposes. It is likely, from consulting the literature, that the last DTA peak at 775^{o}-$820^{o}C$ is that of a carbonyl group. Puri and others identify the properties of high-temperature-activated carbons as being due to the presence of only carbonyl groups, and decomposition is reported as being above $750^{o}C$.

It is also possible that any carbonyls formed during activation may actually be hydrated to hydroxyl or other groups after activation because of the long standing times in wet atmospheres.

The surface oxides which impart activated carbons with most of their unique properties also cause difficulties in determining those properties. The adsorption of water had led to erroneous results in earlier evaluations on this project and in the literature. With the help of the TGA and DTA experiments it was decided that the water was physisorbed, most likely by hydrogen bonds. Therefore the water could be and was removed by heating to temperatures just above the boiling point.

Titration experiments were done on carbons which had been equilibrated with solvent vapor (ethanol vapor in the case of the ethoxide titrations and water in all other cases) and therefore would not adsorb further solvent upon introduction to the titrating solutions. The amount of carbon was determined by drying to a constant weight loss at 110^{o}-$120^{o}C$.

The removal of cations by the electrochemically reduced carbon electrode is the result of both redox and ion-exchange reactions. The redox reactions involve reducible species and alteration of the pH on a local basis to initiate the exchange of Na^+ for H^+ on the acidic surface groups. Thus the ion-exchange and redox reactions are coupled together for the net removal of cations.

During the demineralization phase the oxidation reaction of the silver, silver chloride electrode is:

$$Cl^- + Ag \rightarrow AgCl + e^- \tag{13}$$

with the removal of chloride ions from solution.

The changes in effluent pH and the amounts of surface oxides indicate that the cation removal is by ion-exchange with the acidic carboxyl groups and that not even all of the carboxyl groups are used in the demineralization process. For readily exchangeable groups the carbon electrode has a determined limit of 1.4 ±0.1 meq/g, the amount of carboxyl groups on N:G (2:1) MA. From the discussions of graphite and charcoal it is obvious that the charcoal has most of the reactive oxides. Mixed-acid treated Norit A should have above 1.4 meq/g of carboxyl, and this was indicated as the point of inefficiency in electrode operation at Rocketdyne Corporation as being up to 1.7 meq/g (65, 67).

In the presence of O_2 the electrochemically reduced species are oxygen and water to give an overall inefficient generation of excess hydroxide ions:

$$e^- + \tfrac{1}{2}O_2 + H_2O \rightarrow 2OH^- \qquad (14)$$

$$OH^- + COOH + Na^+ \rightarrow COONa + H_2O \qquad (15)$$

The rate of hydroxide generation exceeds the rate of carboxyl neutralization and cation removal; thus the effluent pH rises to high levels, as was shown in Figure 21.

In the absence of oxygen the reduced species are not so readily identified. The effluent pH still goes basic during demineralization but to lower levels. The electrochemically reduced species could be water, as in the following:

$$e^- + H_2O \rightarrow \tfrac{1}{2}H_2 + OH^- \qquad (16)$$

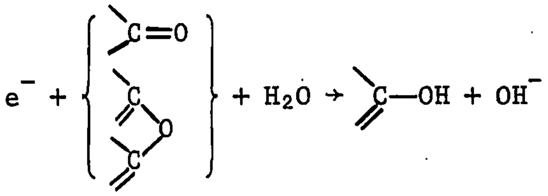
$$OH^- + COOH + Na^+ \rightarrow COONa + H_2O \qquad (17)$$

The adsorption of the hydrogen onto the carbon would provide an oxidizable species which would produce an acid situation upon reversal of the polarity across the cell and thus become the mechanism for regeneration of the salt:

$$\tfrac{1}{2}H_2 \rightarrow H^+ + e^- \qquad (18)$$

$$COONa + H^+ \rightarrow COOH + Na^+ \qquad (19)$$

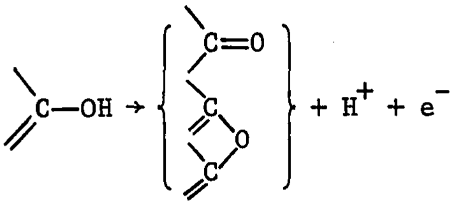
All of the above net reactions could also be accounted for by the presence of a redox group on the surface of the carbon which is reduced during demineralization:



(20)

$$OH^- + COOH + Na^+ \rightarrow COONa + H_2O \qquad (21)$$

and oxidized during regeneration:



(22)

$$H^+ + COONa \rightarrow COOH + Na^+ \qquad (23)$$

The redox group would not enter into the cation removal directly but would essentially act as a site for hydroxide and hydronium ion generation. The pKa of the intermediate >COH would be too high for it to behave as an ion-exchange group towards Na^+, as was stated previously for phenolic hydroxyl groups.

There is not sufficient evidence to be able to decide which of the latter mechanisms accounts for the demineralization-regeneration behavior of the carbon electrode when oxygen is not present.

Chloride ions are, of course, regenerated to the effluent stream by reduction at the silver, silver chloride electrode upon reversal of the polarity across the cell:

$$e^- + AgCl \rightarrow Ag + Cl^- \qquad (24)$$

All of the present studies have been conducted on the cation-responsive N:G (2:1) MA. There have been other electrodes which also performed well. Anion-responsive electrodes constructed from carbon have been made and used in connection with the demineralization project, even though the anion capacity is only about one-fourth the cation capacity of N:G (2:1) MA.

Previous studies on this project and a project in the Engineering Department of Oklahoma University have shown that cells with both cation- and anion-responsive carbon electrodes will perform satisfactorily as demineralization units for saline water (61, 63, 68). The anion electrode was untreated Norit charcoal and graphite with 5% by weight of ethylenimine and the cation electrode was N:G (2:1) MA. The cell consisted of fifteen pairs of 8" x 20" electrodes with 600 mv per pair in an electrical series arrangement. The cell would remove Na^+, Ca^{++}, Mg^{++}, Cl^-, $SO_4^=$, HCO_3^-, and some NO_3^- and $PO_4^{\equiv}$ from both natural and synthetic brackish waters. Iron and manganese, if found in brackish waters, are adsorbed but do not desorb readily from the electrodes. There was some evidence of ion selectivity, as would be expected from a process based upon ion-exchange, so that the amounts adsorbed depended upon the presence of other ions.

The cation-responsive carbon electrodes actually behave as ion-exchangers due to the carboxyl groups imparted to the surface from activation with concentrated sulfuric-concentrated nitric acids. Other oxides are also present on the carbon surface, mostly as phenolic hydroxyl groups. The role of the latter in the demineralization-regeneration process is not known, but they may act as sites for redox reactions with water. The redox reactions involving water are responsible for the pH changes that initiate the ion-exchange reactions, in the constant potential arrangement with silver, silver chloride as the anion-responsive electrode.

Some of the engineering studies on demineralization units containing carbon electrodes are being continued at the University of Oklahoma School of Engineering while the present studies on the carbons themselves are being terminated at this time.

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