POLYELECTROLYTE CONDITIONING

OF

FERRIC SULFATE SLUDGE

by

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I. INTRODUCTION

Water treatment plant sludges are pollutants. When discharged
to a natural receiving stream or impoundment, they produce dynamic
biological, esthetic, and economic effects. The biological effects
are exemplified by a decrease in fish spawning areas, a death by
smothering of purifying organisms on stream bottoms and a chemical
imbalance upsetting the entire ecological system. Unsightly sludge
deposits that are readily stirred up by currents are an esthetic
problem which in turn lead to an economic problem. This economic
problem can be shown in the increased water treatment costs for
municipalities downstream from the discharge point. The argument
frequently expressed that water plants are simply returning wastes
to the water course from which they were removed, holds no weight.
The increased concentration of the wastes alone is reason enough
to justify applying the term pollutant to them and to demand an
acceptable form of disposal.

Sludge from water treatment plant sedimentation and coagula-
tion basins consists of organic and inorganic material, colloids,
plankton, clay particles, microorganisms and precipitates. These
materials are present in quantities that are dependent upon the
raw water source and the time of the year the water is being pro-
cessed. These seasonal variations in the raw water source are both
physical and chemical, thus requiring different coagulant dosages
to be applied in treatment. Filter backwash is composed of a low
solids content sludge consisting of plankton, algae, very fine clay

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particles and some hydroxides of the coagulants being used in treat-
ment. Due to the low solids content of the filter backwash it con-
stitutes more of a hydraulic handling problem rather than a solids
disposal problem, as is the case with the sludge from sedimentation
and coagulation basins. If a plant is using activated carbon to
control a taste and odor problem both the filter backwash and the
sedimentation and coagulation basin sludge will contain large amounts
of this material. The greatest volume of sludge will be found in the
sedimentation basin following coagulation. It is the characteriza-
tion and quantity of this sludge that will be the greatest factor
in determining how ultimate disposal is accomplished by the treatment
plant.

The use of a given material as a primary coagulant will have a
major effect on the nature of the sludge produced. It must be remem-
bered that what applies, for example, to ferric sulfate sludge as far
as a disposal technique, does not necessarily hold true for alum or
sodium aluminate sludge. The sludge from ferric sulfate coagulation
is rather bulky or feathery and is easily affected by currents. Its
color varies from orange-brown to almost black. The consistency of
the sludge is somewhat gelatinous. It does not settle well and as a
result, it does not readily dewater into a sludge cake. The solids
content of the sludge is very low ranging from 0.2 to 5.0 per cent,
and as would be expected varies with the depth in the basin.(1) In
one case the concentration of solids on the surface of the sludge
layer was 1.5 per cent, 10 per cent in the mass center and 14 per

cent on the bottom.(2) It should be noted that most of the total
solids content is measured as suspended solids. The chemical
oxygen demand values for the sludge are comparable to those of alum
sludge which range from 500 to 15,000 mg/1.(3)

With the enactment of the present Federal policy of nondegra-
dation of water courses in the United States, water treatment plants
are now forced to find suitable methods of disposal for their
sludges. Previously sludge has been disposed of in any manner that
was convenient for the treatment plant usually by discharge into the
nearest water course or some kind of crude lagoon system with the
supernatant being subsequently discharged to the water course. In a
random survey conducted by Dean in 1953, he found that out of 1,530
water plants, 92.4 per cent simply disposed of their sludge by dis-
charging it into streams or lakes without treatment.(4) State and
Federal officials were aware of this situation but did nothing about
it, unless some unsightly condition arose and they were forced to
act. It was only in large metropolitan areas where disposal to a
stream was very unattractive in the public eye that some other form
of sludge disposal was used.

In the United Kingdom during this same time, methods of sludge
disposal were being practiced to the fullest extent. These methods
were initiated primarily due to the fact that water shortages were
already starting to exist, and pollution was obvious. It was not
until the middle 1960's that controls on sludge disposal started to
appear in the United States. With the enactment of the Water Quality

Act of 1965, water treatment plant sludges became regarded as industrial pollutants.

In a questionnaire survey of water treatment plants in one hundred different cities in 1968, the conclusion of the Washington Aqueduct Division was that 57 per cent of the plants still relied on discharge to surface streams while only 11 per cent used simple lagoons with no other form of treatment.(2) Later in 1968 State and Federal officials started to enforce the Water Quality Act of 1965, and within the last year water plants have been forced to improve their sludge disposal methods. As an example, Virginia has made the water plants within the state submit reports on their disposal methods and what they plan to do to improve them by the compliance deadline of July 1, 1972.(5) The Ten States Standards for Water Treatment also includes a requirement that disposal methods of sludge from water treatment plants comply with the State Water Pollution Control Agency program of nondegradation.(6)

As a result of the tightening of controls on water treatment sludge disposal, a new problem has arisen. The problem can be simply stated that little research has been done in the United States on disposal methods for water treatment sludges. The Federal Water Pollution Control Administration along with private enterprise has acted in an effort to relieve this deficiency by offering grants to universities and individuals working in this area. The purpose of this research is to help in correcting the deficiency stated above, especially in the area of ferric sulfate sludge.

The Carvins Cove Water Filtration Plant in Hollins, Virginia, has a capacity of eighteen million gallons per day and uses ferric sulfate and lime as coagulant aids. The ferric sulfate sludge from this plant is discharged to a lagoon. The purpose of this research was to characterize the sludge and to determine which polyelectrolytes are best for conditioning it for rapid dewatering. The effect of applying the conditioned sludge to sand beds as a method of disposal has also been investigated. The results also establish the tests which best describe the effects of polyelectrolytes on ferric sulfate sludge and show the suitability of sand beds as a method leading to disposal of the conditioned sludge. In addition, the mechanism by which the conditioning process is accomplished is postulated.

II. LITERATURE REVIEW

In order to consider the possible potential of polyelectrolyte conditioning of ferric sulfate sludge many diverse topics must be investigated. A summary of the important literature in several of these areas is included in the following sections.

Sludge Disposal Methods

Various methods have been suggested, tested, and used for the treatment of water plant sludges resulting from use of ferric sulfate, alum and other coagulants. Since direct discharge to surface streams is no longer acceptable, it will not be considered. Alum recovery and recalcination will not be discussed either, since they are not in themselves methods of disposal. A partial list of applicable techniques includes:

(1) lagoons

(2) discharge to sanitary sewers

(3) centrifuging

(4) freezing

(5) vacuum filtration

(6) sand bed and wedge wire drying

(7) filter pressing

(8) barging

Lagoons are built by simply encircling a piece of land with dikes or mounds resulting from excavation. No underdrains are added to improve drainage, and sludge is pumped into these man-made ponds con-

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tinuously or intermittently. Lagoons are relatively inexpensive
to construct, but their land requirements are excessive, thus often
eliminating them as a method of disposal for urban water treatment
plants. They have been used economically to a great extent in
rural areas. Usually several lagoons are built either in series
or parallel, with flash boards to allow the supernatant to be
drawn off. Problems that may arise with lagoons are associated with
odors, insect breeding and climatic factors that affect the thicken-
ing of the sludge. The two basic ways of operating a lagoon are
by continuous filling or by fill and dry lagooning. Continuous
fill lagooning is used more frequently than fill and dry lagooning
which requires a larger area and also needs more research to per-
fect it.

Lagoon operation has exhibited varying degrees of success.
The tendency has been to avoid deep lagoons because the sludge never
seems to dry out as it does in shallower lagoons. Alum sludge does
not dewater well in some lagoons. One investigator reported that
after several years of settling, alum sludge had a solids content
of only 9 per cent.(7) In other lagoons, sludges have been concen-
trated to 15 per cent solids, a level which enables them to be han-
dled for ultimate disposal.(8) Some plants have reported success
to the extent that the sludge dries sufficiently to allow one to
walk on it after a short period of time. Lagoons in cold climates
have obtained solids contents of a reported 17.5 per cent due to
freezing and the subsequent removal of water of hydration of the

aluminum hydroxide.(2) Ferric sulfate and other sludges tend to

dewater much more readily than alum sludges, thus justifying lagoo-

ning of these sludges. Although it is widely used as a disposal

method itself, a lagoon can also be used very effectively as a pre-

thickening method prior to the application of a mechanical process

to the sludge for further dewatering. Treatment costs for lagooning

vary depending upon the sludge and the cost of the land. If it is

assumed that the lagoon will not be cleaned when it is retired from

service, a value of $40.00/ton of solids removed has been suggested

as an average price.(8) With these ideas in mind, lagooning, which

is currently the most widespread disposal method, would be an accep-

table method only when the price of land is low, the sludge settles

well, no odors are produced and the climate is suitable.

Sludge disposal to a sewage treatment plant has come into use

only recently as a result of the increased knowledge of its effect

upon the treatment plant. By disposing of the sludge to sanitary

sewers one is simply transferring a waste disposal problem to that

facility. For this type of disposal, there are several factors that

must be considered. First, the effect of the sludge upon the sewer

lines must be considered in terms of both chemical and physical pro-

blems. It is doubtful that a sludge will have any noticeable effect

on the sewer chemically, but it has been observed in the city of

Detroit that a velocity of 2.5 feet per second had to be maintained

in order to prevent settling of the sludge.(3) Where sewer line

capacity is lacking, it is possible to discharge the sludge from a

holding tank to the sewer during the hours of low flow. Construction of a sewer line directly from the water plant to the sewage treatment plant has also been done. Secondly, after the sludge has reached the sewage plant, the effective required increase in volume for sludge digestion, storage and ultimate disposal must be considered. In the long run, however, sewage plants may benefit, for some specific sludges actually act as coagulant aids in the treatment of sewage. Lime sludges have been used to aid coagulation for vacuum filtration while the alum sludges have been successfully employed to neutralize acid wastes in sewage treatment plants.(3) The city of Detroit has found water treatment sludges very beneficial in sewage treatment only if they are applied to the sewage plant continuously and in small amounts. They have found that slug disposal of the sludges to the plant caused considerable problems.(2)

For this type of disposal to be effective it is necessary that the sewage plant be of greater capacity than the water plant. If this situation does not hold true, the needed increase in equipment at the sewage plant makes this method of disposal uneconomical. A major drawback associated with this type of disposal method has been the resistance of sewage plant operators to consider this method, especially when the water and sewage works are under different ownership. Many cities have overcome the stated problems and considerations, and in a recent survey 8 per cent of the water treatment plants used sanitary sewers as a method of disposal.(2) Average costs for this method are impossible to obtain due to the many vari-

ables that exist.

Centrifuging has been practiced to a great extent in the United Kingdom where it has been the subject of much research. The process of centrifuging requires some form of settling basin or tank where the sludge can be thickened before it is discharged to the centrifuge. At the Mid-Northamptonshire Water Board Works in England, the sludge is held in holding tanks and then withdrawn to the centrifuge. Two 30 horsepower variable speed centrifuges are used to treat the inflowing sludge at a rate of 3,000 gallons per hour and a solids content of about 10 per cent. The resulting cake produced averages between 65 and 83 per cent solids and is discharged to a conveyor belt which takes the sludge to waiting trucks for final disposal.(9) In the United Kingdom centrifuging is the only process that has been found to be entirely automatic and continuous. Plants in the United States have been hesitant to use this method for disposal, primarily because of the capital cost involved per machine plus the burden of maintenance. The fact that some sludges do not produce a very good cake has been a deterrent for some plants. Austin, Texas, one of the cities currently using this method has had great success. A 40 by 60 inch centrifuge plus accessories was bought in 1965 at a cost of $100,000. Sludges at Austin have been dewatered at a rate of 200 gallons per minute to yield a solids content of 10-15 per cent. Due to the many benefits associated with this method such as little space requirements, little supervision and good stability of the sludge, many more plants will undoubtedly consider this method.

Almost all of the hydroxides formed during coagulation contain a large amount of water of hydration which can be released by freezing. As a result of the removal of the water of hydration, the sludge is transformed from a very gelatinous state to a more stable condition. The effects of freezing can readily be observed in sludge lagoons in very cold areas that are subjected to freezing and thawing. After the freezing and thawing process, the sludge has a coffee ground appearance, and its solids content has increased tremendously. Again the British have taken the initial steps in this area of sludge disposal. The Fylde water plant in England was the first to use freezing as a method of disposal. The entire disposal system consisted of slow stirring to thicken the sludge followed by storage and finally freezing and thawing to a stable state. The freezing is accomplished by passing ammonia refrigerant through coils in a batch tank containing the sludge, while thawing is accomplished by using the same coils as a condenser. The cycle times for the sludge vary between 50 and 120 minutes. The initial capital costs of this method are very high, averaging $17,000/1,000 gallons of sludge(2) frozen a day while the power requirements are between 180 and 230 kilowatt-hour/1,000 gallons of sludge frozen.(9) Freezing can economically be applied only in combination with lagooning of sludge in cold climates, for the present cost of batch processes such as that described above are too high to be justified.

Vacuum filtration of water treatment plant sludges is basically the same process that is used in the dewatering of sewage sludges.

A vacuum filter consists of a cylindrical drum covered with a porous fabric made of cotton, synthetic cloth, metal mesh or steel coils. This cylindrical filter then dewaters sludge through use of a vacuum of about one pound, forming a cake that is suitable for handling and direct disposal upon land. Since alum and other coagulant sludges tend to cause clogging on the filter, a diatomaceous earth precoat may have to be applied to the filter, or the sludge itself may have to be pretreated with lime or a polyelectrolyte before filtration. Lime-softening sludges on the other hand are filtered very easily without any clogging problems. Regardless of the sludge, the process will not work if a dilute sludge such as that associated with continuous sludge removal is brought into contact with the filter material. Due to a new modacrylic fiber woven into filter cloths, the run of a filter cloth can now be extended to six months.(2) Prior to the introduction of this new filter cloth one of the main disadvantages of this method had been the short life of a filter cloth.

In Virginia, a survey of plants using vacuum filtration indicated that it was very effective on prethickened sludges. Capital costs for the plants ranged between $2,800 and $64,000 per million gallons per day of plant capacity for a 32 million gallon per day and a 1 million gallon per day plant respectively, while operating costs for these plants ranged from 2 to 2.8 cents/1,000 gallons of raw water processed.(5) Johns-Manville, working with a precoated vacuum filter in an Albany treatment plant, has successfully ob-

tained a 32 per cent solids cake from a 1.5 per cent solids sludge.
The cost of this process was given as $3.96/1,000 gallons of sludge
treated.(8) From results obtained throughout the United States and
United Kingdom, vacuum filtration of unconditioned alum sludges
seems economically impossible, while other thickened sludges could
possibly use this type of treatment.

Sand beds similar to those used in sewage sludge dewatering
have proven very applicable to the dewatering of water treatment
sludges. Most beds consist of 6 to 12 inches of sand ranging in
size up to 0.5 millimeters with an underdrain system of 6 to 12
inches of gravel overlying drain pipes.(3) The filtrate that is
captured by the drain tile can be recirculated to the raw water in-
take of the plant or discharged to a surface water course. The
sludge is usually applied in shallow layers so that when drying
and cracking occurs, the cracks will extend to the sand surface,
thus increasing the rate of dewatering. Due to the large area
required for these beds, rural areas seem the most likely place for
application of this method. The sand for these beds can be quite
expensive. Additional cost is incurred if the beds are covered. Re-
sults of sand bed drying have much promise. In bench scale tests
with alum sludges it was concluded that in 70 to 100 hours, a
sludge solids concentration of 20 per cent can be obtained.(3) Simi-
lar results have also been obtained in actual field use.

In a Colorado Springs water treatment plant, sludge from sand
drying beds is used in a land fill, while the filtrate from the beds

is so low in suspended solids that it is discharged to a receiving stream.(10) Sand beds do present some problems, such as high labor cost for removal of dried sludge from beds and improper dewatering in cold rainy climates. In the survey of Virginia's water treatment plants by Sutherland, operating costs varied from 0.1 to 2.6 cents/1,000 gallons of raw water treated for a 32 million gallon per day and a 1 million gallon per day plant respectively.(5) Capital costs ranged from $4,700/million gallon per day to $20,000/million gallon per day for the same plants. These costs indicate good economic potential for this method.

Wedge wire drying is similar to sand drying beds and has been used to a very limited extent in the United Kingdom. This method uses mesh sizes ranging from .125 to .25 millimeters in size as the filter media.(3) Sludge has been applied at a depth of from 6 to 12 inches. The process requires traveling covers over the beds due to the fact that they must not get wet during the first week or proper sludge dewatering will not take place. After this covered drying period, the beds are uncovered and the drying continues for three weeks or more until stabilization results. Much more research is required on this method, and as of yet the British have been very hesitant to use it to any great extent.

Filter pressing has been used almost entirely in the United Kingdom, and is largely unknown in the United States except for some pilot batch processes at several large cities. The filter press utilizes hydraulic pressure in the dewatering of the sludge. This

method is a batch process. After the sludge has been put into the press, pressure is applied for varying lengths of time depending upon the sludge being processed. When the sludge has dewatered sufficiently the pressure is released and the sludge cakes fall from the filter cloth onto a conveyor belt and then to waiting trucks. The main objections to this process have been the lack of automation in removing sludge from the filter cloth, and the shut down time required to do this. The process has high initial capital costs as well as high operating costs, but the actual dewatering results obtained have been excellent. In the United Kingdom, prethickening of the sludge is accomplished by stirring or by the addition of chemicals followed by pressing with, typically, a 100 cubic foot press. (9) The press has been found to dewater a 1.8 per cent incoming sludge to a cake containing 25 per cent solids in a pressing time of about 8 hours. Various other plants have indicated the same good results. If more research is done in this field to automate the process and find a more suitable means of handling or disposing of the cakes, this method could be applicable to many situations.

Barging consists of nothing more than pumping the sludge from the plant to a barge which takes it several miles out to sea. The sludge is then pumped from the barge to the ocean floor. This method has proven very advantageous to cities near or on the ocean. Prethickening of the sludge in a lagoon or tank to a suitable solids content would be necessary in order to make this process economically possible. The Northeast Sewage Treatment Plant at Philadel-

phia prethickens its sewage sludges in lagoons to a solids content of 6.5 per cent before it barges them 110 miles down the Delaware River to a disposal site 10 miles at sea.(2) The District of Columbia is considering a similar disposal technique for its water treatment sludges. Care must be exercised in choosing the disposal site to prevent causing damage to fishing and shellfish areas. This process of disposal ceases to be economically justifiable when the distance to the disposal site becomes too great.

Flocculation and Coagulation Theory

Chemical coagulation of raw water prior to filtration is accomplished by the use of such primary coagulants as alum, lime and ferric sulfate. By the use of such coagulants, color, organic and inorganic turbidity, bacteria, taste and odor producing substances and algae can be removed. The theories of coagulation and flocculation that have been developed in water treatment are now finding new application in industrial waste treatment and in water treatment plant sludge disposal.

In the coagulation of colloidal particles there are two basic steps involved: (1) transport of the particle which in turn results in contact with other particles and (2) particle destabilization which enhances attachment when contact occurs. Transport of the particle is strictly a physical phenomenon that is caused by fluid movement or Brownian movement. Particle destabilization on the other hand is a colloid-chemical reaction that can be affected by physical and chemical properties of the liquid, colloid or coagu-

lant.(11) Although there is agreement on the processes involved in

the transportation of the particle, there are differences of opin-

ion on the mechanism involved in particle destabilization. La Mer,

who has done considerable work in this area, breaks particle desta-

bilization down into two categories: (1) reactions that cause a

reduction in the potential energy of interaction between the double

layers of the two particles, and (2) reactions that cause the forma-

tion of chemical bridges that result in a three dimensional floc

network of particles. The first category is exemplified by the

charge neutralization caused by the addition of an electrolyte of

opposite charge and is termed coagulation. The term applied to the

second category is that of flocculation and is demonstrated by the

destabilization of a negatively charged colloidal dispersion by an

anionic polyelectrolyte.(12) A knowledge of the colloidal parti-

cles present in a dispersion is necessary in order to understand

the mechanisms of destabilization that occur.

In the coagulation basins of a water treatment plant two basic

types of colloidal particles exist: (1) those which were formed by

the addition of the coagulant aids and (2) those present in the

raw water initially. These particles vary chemically and physi-

cally to a large degree. The charge possessed by each colloidal

particle is dependent upon several factors.(13) The charge may

be the result of an ionization of one of the functional groups on

the surface of the particle, for example, a carboxylic or hydroxyl

radical may be formed. Adsorption of ions from solution as well

as isomorphic substitution can also help determine the charge existing on the particle. As stated before, in destabilization chemical reactions occur between the reactive groups resulting in the formation of complexes with the coagulant aids, as well as counter-ion adsorption by the colloidal particles.

Adsorption of hydrolyzed coagulant species on the surface of colloidal particles is very important. Some species are more sorbable than others. The sorbability of a certain species is reflected in the concentration of the species that is required to produce destabilization. As would be expected to cause destabilization, species that are adsorbed readily are required in only small concentrations. Chemical bonds will also be formed during this adsorption.(11)

Polyelectrolytes tend to destabilize colloidal dispersions at very low concentrations, while simple electrolytes are required in considerable concentrations in order to effectively cause destabilization. Hydrolyzed metal ions which are formed from the simple metal ions of coagulant aids tend to fall into an area between polyelectrolytes and simple ions.(11) It should be noted that the sorbable species that destabilizes the colloidal dispersion at low concentrations may restabilize it at higher concentrations. This effect only occurs if the species and the particle are of opposite charge.

Ferric Sulfate as a Coagulant

Stumm and Morgan have emphasized that the effects of ferric

and aluminum salts upon coagulation are brought about by the hydroly-
sis products of the salts and not by the simple aquo-metal ions them-
selves.(13) This hydrolysis is accomplished by a stepwise consecu-
tive replacement of water molecules in the hydration shell by hydro-
xide ions. For example:

$$Fe(H_2O)_6^{+++} \longrightarrow Fe(H_2O)_5OH^{++} \longrightarrow Fe(H_2O)_4(OH)_2^{+} \longrightarrow$$

$$Fe(H_2O)_3(OH)_3 \longrightarrow Fe(H_2O)_2(OH)_4^{-} . (11)$$
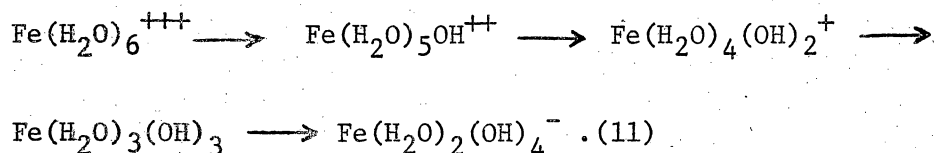
The products of this hydrolysis are termed multinuclear hydroxo-metal
complexes and are usually highly charged. The complexes can be
nonionic, cationic or anionic depending upon the species existing.
Some of the species formed in the hydrolysis steps tend to polymer-
ize.

Spiro confirmed the existance of a hydroxo ferric polycation
formed by the above mentioned polymerization step with a molecular
weight of 1.4×10^5.(14) The charge and structure of the products
of hydrolysis were dependent upon the pH of the water being treated.
It should also be noted that the addition of any iron salt to
water will result in a decrease in pH and alkalinity. Stumm and
O'Melia have concluded that after the hydrolysis has been completed
the following steps will then occur in the time dependent coagula-
tion mechanism: (1) adsorption of the hydrolysis species into the
colloidal particles followed by destabilization; (2) the destabi-
lized colloidal particles then aggregate and interparticle bridging
occurs; (3) aging of the flocs that were formed leads to a chemical

change in the multinuclear hydrolysis products and the sorbability

of the floc; and (4) precipitation of the metal hydroxide is com-

pleted.(11)

Ferric sulfate is a light red-brown powder with particles up to

one-eighth of an inch in diameter. Upon the addition to water the

powder becomes deep red-brick in color. The powder is manufactured

from air-floated ferric oxide and sulfuric acid, and is usually hy-

drated to some extent in order to insure that solution with water

will be relatively quick at normal temperatures.(15) Although the

powder may vary, the general formula is $Fe_2(SO_4)_3 \cdot 9H_2O$. Ferric

sulfate was first used in the United States in 1927, at Elizabeth

City, North Carolina, as an effective way of removing color from

raw water.(16)

In water treatment ferric sulfate is used for three basic rea-

sons: (1) color can be removed very economically and efficiently by

proper coagulation with the salt; (2) the salt is more effective

than alum or lime in destabilizing a colloidal dispersion containing

significant amounts of iron; and (3) manganese can be successfully

removed by the salt in the pH range from 9 to 10. The flocs pro-

duced in ferric sulfate coagulation are heavy, tough and tend to

filter and settle much better than alum or lime flocs. The pH range

for coagulation with the salt is quite broad, ranging from 3 to 10.

Black, et al., have found that color removal with ferric sulfate

is optimum at a low pH of about 3.5. The water must then be par-

tially neutralized to a maximum pH of 6 before filtration in order

to get effective color removal.(17) The effluent produced from

ferric sulfate coagulation in most cases has a residual iron concen-

tration less than the maximum allowable by the United States Public

Health Service Drinking Water Standards.

Polyelectrolytes

Polyelectrolytes have a high molecular weight, are water soluble

and are classified as either natural organic or synthetic organic

compounds. They have been used many years in industrial processes,

but it has been only recently that they have been employed in sludge

conditioning and water treatment. Synthetic polyelectrolytes are

structurally very much like naturally occurring polyelectrolytic

colloids. They are essentially polymerized ions and contain reactive

groups such as carboxylic acids, hydroxides and amines.

Stumm and O'Melia have stated that destabilization of colloidal

dispersions by polyelectrolytes can not be explained through the dou-

ble layer model, but instead a chemical bridging or flocculation

theory must be used.(13) La Mer and coworkers were the first to

propose a mathematical model of the chemical bridging theory to

explain the action of polyelectrolytes in destabilization of colloi-

dal dispersions.(12) Earlier work on the chemical bridging theory

was done by Ward and Ruehrwein. Through their tests dealing with

the adsorption of polymethacrylate on kaolinite clay dispersions

they helped establish and confirm the chemical bridging theory.(18)

Since this early work, much more data has been obtained to support

the chemical bridging theory of polyelectrolyte destabilization.

Bugg, in his research on the conditioning of alum sludges with poly-

electrolytes, also concluded that the chemical bridging theory satis-

factorily described the mechanism involved in the conditioning of

this sludge.(19)

The chemical bridging theory states that polyelectrolyte mole-

cules may attach themselves to colloidal particles at one or more

adsorption sites. The remainder of the molecule that is not attached

extends out into the solution containing the colloidal particles. If

this extended segment makes contact with a colloidal particle it be-

comes attached to it. As this process continues for the many extended

segments of one polyelectrolyte molecule bridges are formed between

colloidal particles. If adsorption is effective for all the poly-

electrolyte molecules present, the net result is that the colloi-

dal particles are aggregated into small packages that continue to

grow in size. Factors limiting this growth are the amount of poly-

electrolyte initially adsorbed on the surface, and the shear gra-

dient imposed by the amount of agitation necessary in promoting par-

ticle-polyelectrolyte contacts. The many extended segments of each

polyelectrolyte molecule are usually free of relative mutual inter-

actions between themselves. When too many adsorption sites are

occupied by polyelectrolyte extended segments, bridging will be in-

hibited. In a like manner if too few adsorption sites are occupied

by the segments, bridging will be very weak and agitation will rea-

dily destroy the floc. Adsorption usually increases with increases

in molecular weight of the polyelectrolyte. The number and type of

functional groups on the polyelectrolyte molecule will also affect

the adsorption characteristics of the molecule. The Langmuir adsorp-

tion isotherm has been found to be useful in describing polyelectro-

lyte adsorption.(20) The adsorption of the polyelectrolyte mole-

cular segment on to the colloidal particle may be by chemical or

physical interaction depending upon the polyelectrolyte and the col-

loidal particle reacting.

To further help explain the chemical bridging theory the mathe-

matical model developed by La Mer and Healy is presented:

β = Number of segments per polymer molecule adsorbed on avail-
able surface sites.

Υ = Average number of polymer segments per polymer molecule.

$(\Upsilon - \beta)$ = Number of extended segments for each attached polymer

molecule.

β/Υ = Fraction of segments adsorbed.

P = Residual polymer left in solution after adsorption.

Po = Initial polymer added.

N = Avagadros' number.

So = Surface area of the adsorbent.

s = Number of surface adsorption sites per unit area of adsor-

bent.

Assumptions made are that (Po-P) moles of polymer are concentra-

ted at the interface of the adsorbent, and that the polymer segment

capable of adsorption is the same size as the surface site on the

adsorbent. Thus (Po-P)N molecules are concentrated at the interface.

If each polymer has Υ extended segments then $(Po-P)N\,\Upsilon$ segments are concentrated at the interface.

Therefore:

$\beta(Po-P)N\,\Upsilon/\Upsilon$ = Number of surface sites covered on the adsorbent.

$\beta(Po-P)N/sSo$ = θ = Fraction of surface sites on adsorbent covered.

Let:

$K = sSo/N$

Therefore:

$P = Po-K\theta/\beta$

La Mer and Healy have also concluded that destabilization is a maximum when $\theta = 0.5$.(21) As would be expected there is a direct relationship between the amount of particles in the dispersion and the optimum polyelectrolyte dosage required for destabilization.

Black, Birkner and Morgan have found that the kinetics of polyelectrolyte adsorption are very rapid, with 85 per cent of the equilibrium value being adsorbed in only 30 seconds. They have broken the kinetics down into two steps: (1) the rate at which the polymer is adsorbed from solution and (2) the rate at which the initial particles agglomerate to form secondary, tertiary and n-unit particle aggregates.(20) Anionic polyelectrolytes have been found to be readily adsorbed on negatively charged clay particles. Tests with a polyacrylamide by Kane, La Mer and Linford indicated that with increased hydrolysis and negative charge, the polyelectrolyte did a

progressively better job of destabilizing negatively charged silica
particles.(22) Thus anionic polyelectrolyte destabilization is
strictly by flocculation mechanisms. The proposed mechanism for
destabilization by cationic polyelectrolytes on the other hand is a
combination flocculation-coagulation process. The cationic poly-
electrolyte serves first as a coagulant by reducing the repulsive
charges between particles, and then chemical bridging takes place
as the rate controlling reaction.(20) Nonionic polyelectrolytes
exhibit both forms of destabilization shown by the cationic and
anionic polyelectrolytes but to a smaller degree.

Sludge Filterability and Sand Beds

Perhaps the best laboratory test to determine the filterability
or drainability of a sludge is the Buchner funnel test. It has been
used almost exclusively as a control test for the sludge disposal
method utilizing vacuum filtration. The Buchner funnel test mea-
sures the amount of time required for a filter cake to crack. The
test consists of measuring over a time period the production of
filtrate that comes from the cake when a vacuum has been applied.
The filterability of the sludge is expressed by the term specific
resistance which is calculated by the following formula.(23)

$$r = \frac{2bPA^2}{uc}$$

r = Specific resistance of sludge (sec^2/gm).

b = Slope of the plot of T/V versus V (sec/cm^6).

where: T = Time in seconds.

V = Volume of filtrate from sludge in ml in

time, T.

P = Pressure applied, (gm/cm^2).

A = Area of filter, (cm^2).

u = Viscosity of filtrate (g/cm-sec).

c = Ratio of dry cake solids in grams per ml of liquid before

filtration (gm/ml).

The theoretical basis for this test was initially developed in

1933, by Ruth and Carman, but Coackley and Jones later modified the

test to give the procedure that is presently used. In comparing the

effects of different conditioning agents on sludge, they concluded

that the specific resistance or Buchner funnel test was an excellent

measure of sludge filterability.[24]

Gates and McDermott ran specific resistance tests on alum

sludge and recorded values for unconditioned sludge of about 0.1×10^{10}

sec^2/gm. They then conditioned the sludge with various polyelec-

trolytes and again ran specific resistance tests. The conclusions

they drew from their tests were that specific resistance is a valid

measure of the effect of polyelectrolytes on alum sludge, but it is

not a valid basis for predicting the loading rate for vacuum filters

and the associated savings by using polyelectrolytes.[23] Bugg also

worked with polyelectrolyte conditioning of alum sludge and concluded

that specific resistance was a good measure of the effect of poly-

electrolytes on sludge filterability. He recorded specific resis-

tance values for unconditioned alum sludge ranging from 8×10^8 to

11 X 10^8 sec^2/gm.[19]   Little research has been done on the possi-

bility of relating specific resistance to gravity dewatering as

would be the case if the sludge were applied to sand beds.

The types and uses of sand beds as a method of sludge disposal

have already been presented. Eckenfelder and O'Conner described

the method of dewatering by two steps: (1) the filtration of water

from the sludge through the sand to the tile system and (2) the

evaporation of moisture from the surface of the sludge. They found

that the filtration action may last for one to two days and result

in an increase in solids content ranging from 13 to 22 per cent.[25]

Bugg, in his sand bed studies with alum sludge, found that filtra-

tion lasted for two days for a polyelectrolyte conditioned sludge

while filtration in an unconditioned sludge lasted for five days.

His results show a decrease in volume of 46 per cent in one hour for

the conditioned sludge compared to only a 7 per cent reduction in

volume for an unconditioned sludge in 1 hour and 25 minutes. He

also concluded that evaporation rates for both the conditioned and

unconditioned sludge were about the same.[19] It should be noted

that evaporation drying occurs in three stages: (1) a constant

stage when the surface of sludge is entirely wet, (2) a falling rate

stage when the critical moisture content occurs and water lost by

evaporation at the surface is not replenished at the same rate, and

(3) a subsurface drying stage until a final equilibrium moisture

content is reached.[25] Although the design of the beds varies con-

siderably, all work on the basic principles described.

Zeta Potential

Zeta potential is a measure of the electrokinetic charge that surrounds a colloidal particle.(26) It is also referred to as the potential that exists at the plane of shear between the particle and the bulk of the solution. Zeta potential thus describes the forces of repulsion in a colloidal system. As a result of these repulsive forces the particle is kept in solution. The more negative or positive the zeta potential, the more stable the colloidal solution. Most systems of interest in water treatment are negatively charged. In Table I, Riddick indicates how colloidal stability varies with zeta potential for most anionically dispersed systems.(27)

Since zeta potential is proportional to the rate of movement of the colloidal particle in an electric field, it can be calculated by the following formula.(26)

$$ZP = \frac{4 \pi UV_t}{D_t}$$

Where:

U = Electrophoretic velocity of the colloidal particle.

V_t = Viscosity

D_t = Dielectric constant of the suspending liquid.

Most colloids suspended in raw water are electronegative in the range from -15 to -30 millivolts.(28) Recently many new ideas have developed with regard to coagulation of water. Many of these ideas are the result of increased knowledge about the zeta potential of

TABLE I

RELATIONSHIP OF ZETA POTENTIAL TO COLLOID STABILITY (27)

STABILITY CHARACTERISTICS	AVERAGE ZETA POTENTIAL (millivolts)
Maximum agglomeration and precipitation	0 to +3
Range of strong agglomeration and precipitation	+5 to -5
Threshold of agglomeration	-10 to -15
Threshold of delicate dispersion	-16 to -30
Moderate stability	-31 to -40
Fairly good stability	-41 to -60
Very good stability	-61 to -80

colloids. For example, in present coagulation practice the ferric

or alum floc that is formed has a zeta potential in the same range

as the colloids present in raw water. Thus it would seem likely

that the repulsive forces of the floc and the colloidal particle

will prevent them from becoming permanently attached. Riddick feels

that if the zeta potential of the floc and the colloid could be

reduced to approximately zero, better colloid removal would result.

He has proposed the use of an inorganic coagulant dose followed by

the addition of an organic polyelectrolyte in order to obtain a

zero zeta potential. The Waterford, New York, water treatment plant

is run utilizing zeta potential as a control parameter to indicate

proper dosages suggested by Riddick. Very good colloid removal has

resulted at the plant.(26)

Results of the addition of polyelectrolytes in water treatment

indicate that they affect the zeta potential of the colloidal system

greatly without changing either the pH or alkalinity.(26) Since

the polyelectrolyte is normally added after the inorganic coagulant,

it becomes attached to the floc produced by the coagulant. At

dosages above 0.6 parts per million, the anionic polyelectrolytes

tend to increase the zeta potential in a more electronegative direc-

tion, but the chemical bridging mechanism of the polyelectrolyte

more than counter balances this effect.(26) Stumm and O'Melia have

concluded, from their tests using polyelectrolytes as coagulant

aids, that optimum aggregation does not necessarily occur at a zeta

potential of zero.(11) In polyelectrolyte conditioning of alum

sludge, Bugg concluded that a zeta potential of -30 gave the opti-
mum sludge filterability, and that zeta potential became more elec-
tronegative with an increase in anionic polyelectrolyte dosage.(19)

Summary

As can be seen from the literature, while some work has been
done in the field of water treatment plant sludge disposal, much
more research is needed. Most current research has centered around
alum sludge, while ferric sulfate and lime sludges have been vir-
tually ignored. The relationship between specific resistance and
gravity dewatering of sludge needs to be more fully explored. Work
on the conditioning of different sludges with various polyelectro-
lytes has proven very fruitful, but much more research is needed in
this area. The relationship between zeta potential and the opti-
mum polyelectrolyte dosage should be investigated further. The
purpose of this research is to explore the relationships between
specific resistance, polyelectrolyte dose, solids content and system
pH for the conditioning of ferric sulfate sludge. In this work ulti-
mate disposal would be accomplished following vacuum filtration or
sand bed drying.

III.   EXPERIMENTAL METHODS

The test procedures for measuring the effect of polyelectro-
lytes on ferric sulfate sludge must be easily reproduceable and
yet valid indicators of the mechanisms involved in the conditioning
process.   The tests selected for this research exhibit these quali-
ties and thereby enable the results to be applied, to a limited
extent, to other ferric sulfate sludges.

Sampling and Storage

The ferric sulfate sludge used in this research was obtained
at the Carvins Cove water treatment plant in Hollins, Virginia. A
flow diagram of the plant is shown in Figure 1. Although the
capacity of the plant is 18 million gallons per day, actual produc-
tion usually ranges between 11 and 14 million gallons per day. A
chemical analysis of the raw and treated water is shown in Table II.
In Table III a summary of the yearly raw water production and coagu-
lant usage is given along with data concerning filter backwashing
and the application of activated carbon. As can be seen from the
flow diagram of the plant, the method of sludge disposal is by fill
and dry lagooning. The ferric sulfate sludge is removed from the
sedimentation basins twice a year, usually in early spring and fall.
The sedimentation basins are 14 feet deep and slightly sloped to a
sump pump drain at one end. The sludge is removed by manually pushing
it to the sump pump which then pumps it to the lagoon. The average
time for cleaning one basin is approximately 6 hours. The sludge
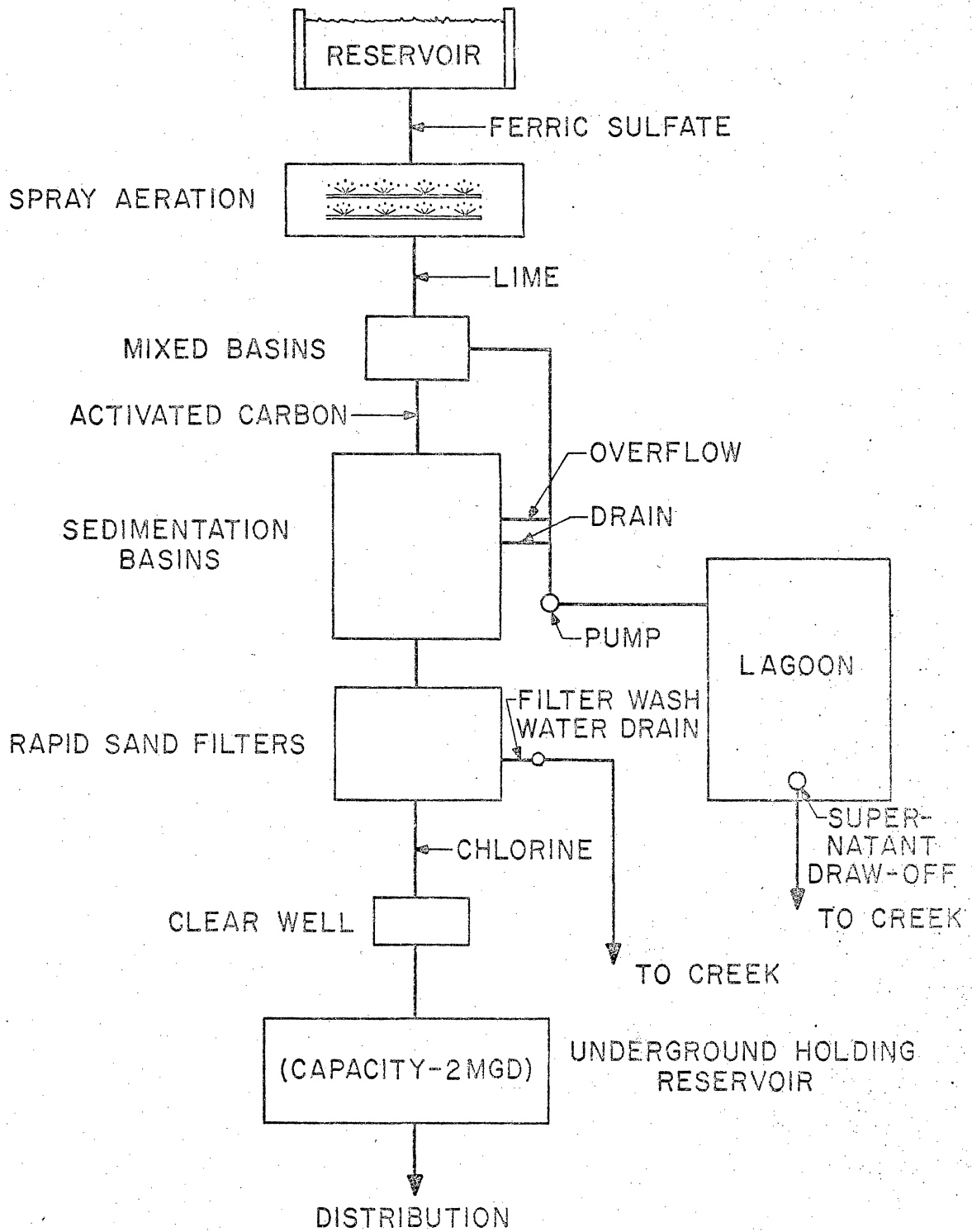
FIGURE I-FLOW DIAGRAM CARVIN'S COVE
WATER TREATMENT PLANT

TABLE II

CHEMICAL WATER ANALYSIS OF CARVINS COVE

	RAW WATER	TREATED WATER
pH	7.8	7.8
Alkalinity M.O. (mg/1)	60	56
Alkalinity P. (mg/1)	0	0
Hardness (mg/1)	66	78
Iron (mg/1)	.01	0
Manganese (mg/1)	0	0
Color Units	0	0.07
Turbidity	1.5	0

TABLE III

ANNUAL WATER PRODUCTION AND COAGULANTS

Carvins Cove Water Filtration Plant

YEAR	TOTAL WATER GALLONS	FERRIC SULFATE POUNDS	LIME POUNDS
1960	1,821,252,000	329,382	289,278
1961	2,272,966,000	439,438	345,475
1962	2,459,190,000	537,932	380,884
1963	2,615,865,000	510,932	388,578
1964	2,712,034,000	521,734	388,071
1965	2,748,580,000	529,733	416,638
1966	3,181,794,000	606,506	465,009
1967	3,014,333,000	567,832	405,921
1968	3,518,938,000	699,813	429,587
1969	3,725,805,000	866,508	436,066
TOTALS	28,070,757,000	5,599,810	3,945,307

NOTE: Volume of washwater averages 5.1 per cent of total
water. Filter beds are backwashed every 35 hours
on the average. 315 pounds of activated carbon is
added per day to control a taste and odor problem.

used in this research was obtained by entering the basin while it was being cleaned and collecting several five gallon samples. The samples were then stored at a constant temperature of $20^{\circ}C$ for a maximum of three weeks while testing was being conducted. Dilution water used to adjust the solids content of the sludge samples was obtained from the sedimentation basins at the plant and stored in the same manner as the sludge sample.

Sludge Characterization

Proper characterization of the sludge from the plant is very important. Only if the sludge is characterized properly can the results of this research be applied to other sludges produced at other plants. The following tests were run to insure that good sludge characterization was obtained.

Total, Volatile and Fixed Solids

Sludge samples were analyzed for total, volatile and fixed solids in accordance with the procedures outlined in Standard Methods for the Examination of Water and Wastewater, 12th Edition.(29) A 100 ml sample was used in each experiment. Samples that were lumpy as the result of polyelectrolyte conditioning were mixed well until homogeneous at a speed greater than 100 rpm by a multiple jar test apparatus manufactured by Phipps and Bird of Richmond, Virginia. The 100 ml sample was then obtained from this homogeneously mixed sample. Solids remaining in the graduated cylinder after the 100 ml sample was poured into the evaporating dish were rinsed from the cylinder

with distilled water and added to the evaporating dish. In order

to obtain total solids the dish was dried for 12 hours on a steam

bath followed by one day in an oven at $103^{\circ}C$. Volatile and fixed

solids were determined by burning at a temperature of $600^{\circ}C$ for 30

minutes.

Chemical Oxygen Demand

Chemical oxygen demand was determined by the dichromate reflux

method as described in Standard Methods.(29)

pH

pH was determined by a Leeds and Northrup pH meter, catalogue

number 7401. Special attention was given to the care and cleaning

of the electrodes with distilled water. Adjustment of pH was

accomplished through the use of concentrated sulfuric acid or 0.5N

sodium hydroxide.

Polymer Solution Preparation

Table IV gives pertinent information concerning the polyelec-

trolytes that were used in this research. As can be seen from the

table certain information was not obtainable from the companies.

Polyelectrolytes from Dow Chemical were already in solution when

received. These polymers were used at the concentrations indicated

in the table. Storage of these polymers never exceeded one month

as recommended by Dow. Nalco 675 was received from Nalco Chemical

Company in solid form. Solution of 675 was accomplished through

heating and the use of a magnetic stirrer. Distilled water used in

TABLE IV

POLYELECTROLYTE DATA

POLYMER	DOW-A-23	DOW-N-17	DOW-C-31	NALCO 675
Charge	anionic	nonionic	cationic	anionic
Physical form	white grandu- lar solid	white grandu- lar solid	dark viscous liquid	white powder
Concentration, weight % used	0.5	1	20	.1
Viscosity (CPS) at 25°C	9,750	475	225	-
Molecular weight	1,000,000+	1,000,000+	-	1,000,000+
Chemical structure	polyacry- lamide	polyacry- lamide	polyethyleni- mine	polyacry- lamide

NOTE: Polymers A-23, N-17 and C-31 were received from the Dow Chemical Company, Midland, Michigan. Polymer 675 was received from Nalco Chemical Company, Chicago 38, Illinois.

making up the solution, was heated to a maximum temperature of 150°F

while the time of agitation by the stirrer was kept less than 30

minutes. A 0.1 per cent solution of Nalco 675 was used in all research

except the sand bed studies where a 0.25 per cent solution was used.

Buchner Funnel - Specific Resistance Test

The Buchner funnel specific resistance test was chosen as the

means of measuring the filterability of the conditioned and uncon-

ditioned ferric sulfate sludge. The procedure and equipment ini-

tially described by Coackley and Jones[24] was later modified by

Bugg.[19] The modified procedure and equipment was used throughout

this research. Specific resistance was reported in sec^2/gm. The

apparatus consisted of a 9 cm. Buchner funnel with a moistened

piece of Whatman No. 40 filter paper in the bottom. A thin layer

of stopcock grease was applied to the bottom of the plexiglass ring

before it was pressed into place around the edge of the filter paper.

When slight pressure was applied to the ring, an impermeable seal

resulted. Bugg found that this seal prevented the finer sludge

particles from escaping around the edge of the filter paper.[19] A

vacuum pump was used to apply the pressure differential of 12 inches

of mercury measured through the use of a manometer. Filtrate from

the funnel was collected in a 250 ml cylinder.

500 ml samples of sludge in one liter beakers were used in the

conditioning tests. The pH of the sample was first adjusted, followed

by the addition of the desired polyelectrolyte dosage. Agitation

during polyelectrolyte addition was accomplished by the use of a
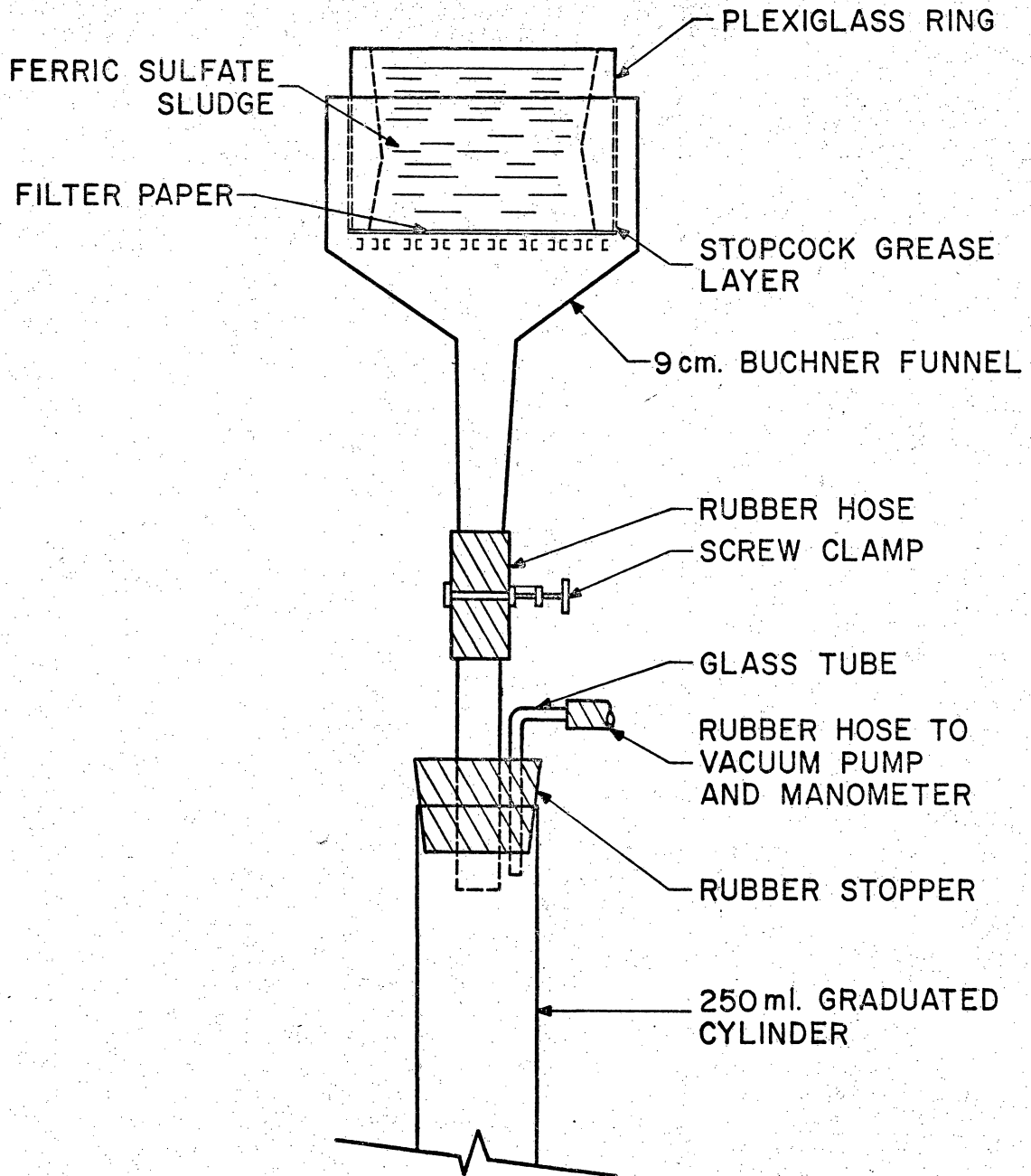
FIGURE 2 - BUCHNER FUNNEL APPARATUS FOR
SPECIFIC RESISTANCE TEST

multiple jar test apparatus running at a speed of 100 rpm for 2 minutes. The flocculation parameter, or G value, during this flash mix period was 148.5 sec^{-1}. The speed and time of the mix were determined by Bugg to be optimum. He concluded that a rapid mix was necessary to prevent the polyelectrolyte solution and the solids which had adsorbed polyelectrolyte from settling out. The rapid mix was also needed to assure a large number of particle-polymer contacts. If the speed and time of agitation exceeded the optimum, the floc structure was found to deteriorate.[19]

After the flash mix a settling time of 15 minutes was allowed. Next the supernatant was drawn off and part of the remaining conditioned sludge was applied to the funnel. Since some of the conditioned samples were very lumpy, no constant volume of sludge was applied to the filter for each test. After application of the sludge to the filter, 10 to 15 seconds were allowed for cake formation by sedimentation. During this time the vacuum pump was turned on and the pressure differential set at 12 inches of mercury. Next the screw clamp between the funnel and the graduated cylinder was opened and filtrate volume readings were taken at different time intervals. Readings for fast filtering samples were taken every 10 seconds for the first two minutes and then every 20 seconds for the remainder of the time. In unconditioned and slow filtering samples, readings were taken every 30 seconds for the first five minutes and then every two minutes for the remainder of the time. The test was continued until the cake cracked, the filtrate volume became constant,

or the pressure differential dropped.

It was noticed that in fast filtering samples a large volume of filtrate passed through the medium during the first several seconds. Coackley and Jones also noted this and concluded that it was caused by insufficient cake formation. They stated that the major resistance was due to the filter paper instead of the cake and proposed that the time and volume readings be corrected. Correction consisted of subtracting the volume collected during the initial seconds from the rest of the volume readings, thus the first reading becomes the zero reading. Time was also corrected in a similar manner.(24) All fast filtering samples were corrected in this manner.

All plots of T/V versus T for slow filtering samples yielded straight lines. Plots for fast filtering samples gave straight lines only after correction. Specific resistance was calculated by the equation indicated in the previous chapter. The parameter c was determined by a total solids test for a 100 ml sample of the remaining conditioned sludge that was not used in the specific resistance test.

Zeta Potential Test

A Standard Zeta Meter, serial number 1238, was used in all zeta potential determinations. The supernatant from conditioned and unconditioned samples was used in all zeta potential tests. Most conditioned sludge samples yielded a rather clear supernatant that could be used as a test sample in the zeta potential determination.

On the other hand, unconditioned and conditioned sludge samples

that did not settle well had to be centrifuged to obtain a rela-

tively clear supernatant. A Fisher Scientific International Clini-

cal Centrifuge, Model No. 28158H was found to be capable of clari-

fying the samples in approximately 5 minutes. The supernatant after

centrifuging was then used in zeta potential determinations. Rela-

tively little solids in the supernatant is a prerequisite to valid

zeta potential readings. For samples containing fast moving parti-

cles, 10 different particles were timed traveling over a one micro-

division distance. An average time for one particle could thus be

determined from these 10 different particle times. Only 5 different

readings were required for samples with slow moving particles. More

detailed information concerning this procedure can be found in the

Zeta Meter Manual.(28)

Bench Scale Sand Bed Studies

Sand bed studies were conducted using plexiglass beds one square

foot in cross-sectional area. The beds were constructed with three-

eights inch plexiglass sides and a funnel shaped plexiglass device

to collect filtrate that had drained from the sludge sample. The

filtrate was then conveyed from the funnel device by a rubber hose to

a 2 liter graduated cylinder where it was measured. The filter

medium consisted of a 1 inch layer of coarse sand, which was retained

on a number 10 soil sieve, covered by a 3 inch layer of light-weight

Weblite aggregate sand with a uniformity coefficient of 2.89 and an

effective size of 0.40 mm. The medium was supported on the bed by

fine wire mesh screens. From the top of the Weblite sand to the
top of the plexiglass side was approximately 9 inches.

14 liter samples at 3.6 per cent solids were used in the stu-
dies. Samples were poured into a 30 liter, wide-mouth pyrex jar
after which the proper polyelectrolyte dosage was added. A 2 minute
flash mix at 100 rpm was accomplished through the use of a variable
speed stirrer manufactured by Inframo of Wayne, New Jersey. After
the flash mix, the sample was quickly applied to the bed. Filtrate
volume measurements were taken at various times during the filtra-
tion action. Moisture content during this period was calculated by
the following procedure:(19)

    (1) Calculate the volume of sludge remaining by subtracting

        the volume of filtrate collected from the total volume of

        sludge applied.

    (2) Calculate the total solids content of the remaining sludge

        by the following equation:

$$\text{Total solids remaining, \%} = \frac{(\text{Total volume applied})(\text{Applied total solids,\%})}{\text{Volume remaining}}$$

    (3) Calculate the per cent poisture of the sludge.

        Per cent moisture = 100 - (Total solids remaining in %)

Two problems with the above procedure are that it assumes that
all the solids are retained on the sand and that no drying occurs as
a result of evaporation during the filtering action. All the data
had to be corrected in order to account for the evaporation during
the filtering action. The correction consisted of determining a

constant evaporation rate from the difference between the calcu-
lated moisture content and the core sample moisture content. This
constant rate of evaporation was then used to correct the data.
After the filtration action had stopped, the air drying rate was
determined by taking core samples of the sludge.

Sand bed studies were run on three polyelectrolyte conditioned
samples and one unconditioned sample. The beds were located on a
window ledge in the laboratory. The windows near the beds were left
open and as a result the beds were subjected to all the changes in
humidity and temperature that occurred outside. The beds did not
have direct sunlight.

IV. EXPERIMENTAL RESULTS

The tests performed during this research resulted in data of significance to the field of water treatment plant sludge disposal. The results of the tests explain the interrelationship between optimum polyelectrolyte dosage and such variables as pH, specific resistance, zeta potential, solids content, polyelectrolyte type, and dewaterability on open sand beds. All of these variables were studied in detail during the research.

Sludge Characterization

Proper sludge characterization is one of the most important steps in obtaining test data that is of value in solving the problem of water treatment plant sludge disposal. Without knowing the characteristics of the sludge being treated, the results are almost meaningless. Data concerning the plant such as its size and type as well as the coagulants used must also be given in order to more fully understand the sludge characterization data. All data concerning the Carvins Cove water treatment plant was previously shown in Table II and Table III as well as in Figure 1. The fact that the plant uses activated carbon to control taste and odor should not be forgotten.(See Table III)

Table V shows the results of the sludge characterization tests that were run on three different samples. Since the samples used throughout the research were obtained during three different sedimentation basin cleanings, a characterization was run on one sample

TABLE V

SLUDGE CHARACTERIZATION

|	SAMPLE I	SAMPLE II	SAMPLE III
pH	7.3	7.4	7.3
Total solids (mg/1)	35,881	36,1831	36,028
Volatile solids (mg/1)	7,212	7,481	7,286
Fixed solids (mg/1)	28,669	28,765	28,742
COD (mg/1)	5,460	5,780	5,543

from each cleaning. Results showed that the characteristics of the

sludge remained basically constant from one basin to another. The

pH of the sludge was slightly more acidic than the pH of the raw

and treated water. (See Table II) Results of the test showed a

sludge that was relatively low in total solids with a high COD value.

Most of the solids present in the sludge were in the form of fixed

solids, although a small percentage of volatile solids did exist.

The possible deleterious effect of the sludge on any receiving

water course is quite obvious from the COD values shown. A COD

determination of a sample of the supernatant from the lagoon indi-

cated a value of 373 mg/l. The supernatant from the lagoon was not

clear due to the rather poor settling qualities of the ferric sul-

fate sludge. A five-day BOD was not run on the sludge or super-

natant since such a test was not deemed valid or necessary.

Effect of Polyelectrolytes on the Specific Resistance

of Ferric Sulfate Sludge

Specific resistance was chosen as the test parameter to measure

the effect of polyelectrolytes on sludge filterability. Cationic,

anionic and nonionic polyelectrolytes from Dow Chemical and Nalco

Chemical were used in these sludge conditioning tests. (See Table IV)

The working solids content of the sludge was chosen as 3.6 per cent

since this was the average concentration at which the sludge was

being pumped to the lagoon. The pH of the sludge ranged from 7.3

to 7.8 with an average value of 7.5. Specific resistance was deter-

mined for each dosage of the polyelectrolyte applied to the ferric

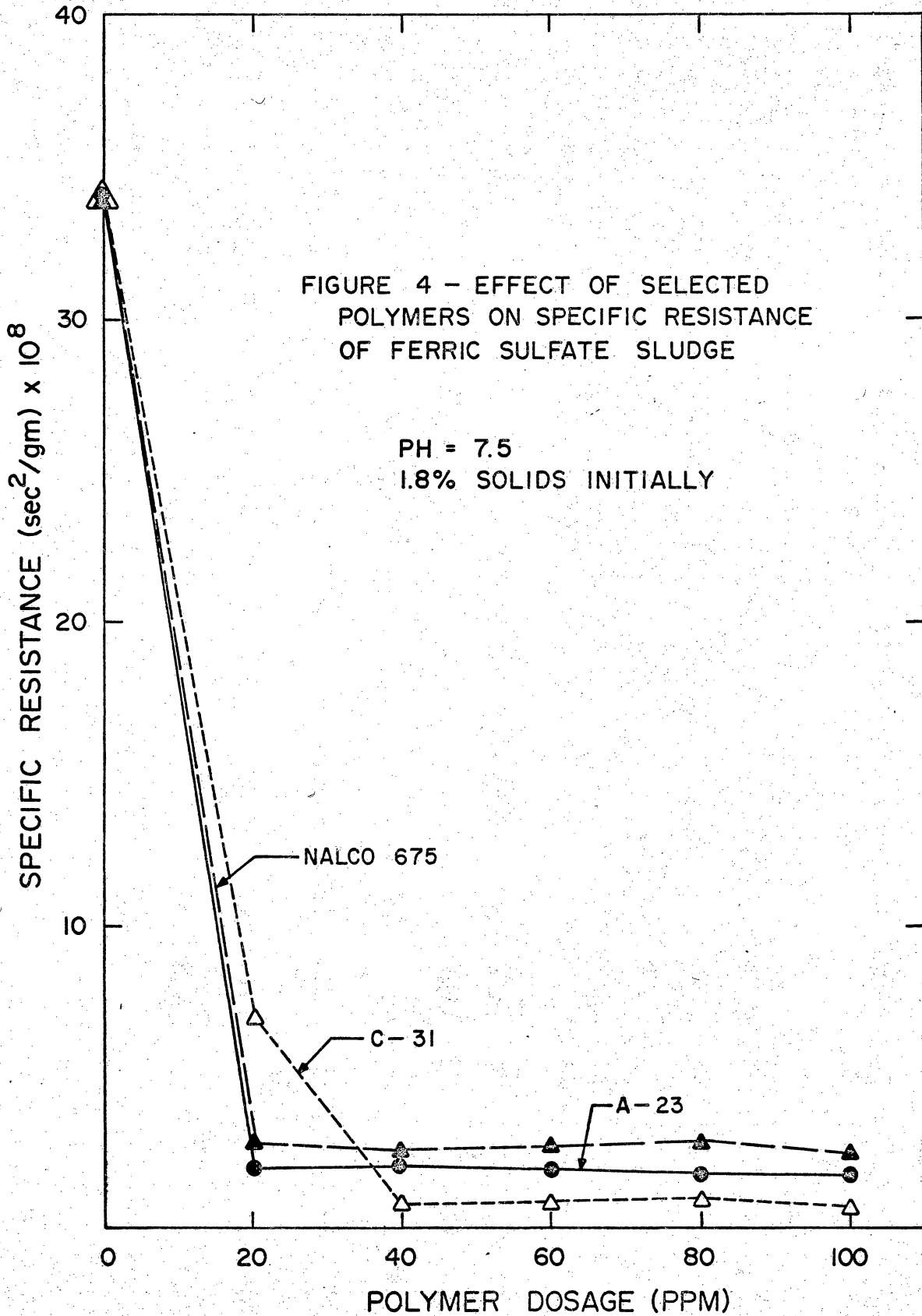sulfate sludge. The optimum polyelectrolyte dosage was established

by the run that gave the lowest value of specific resistance. The
results of conditioning the 3.6 per cent solids sludge are shown in
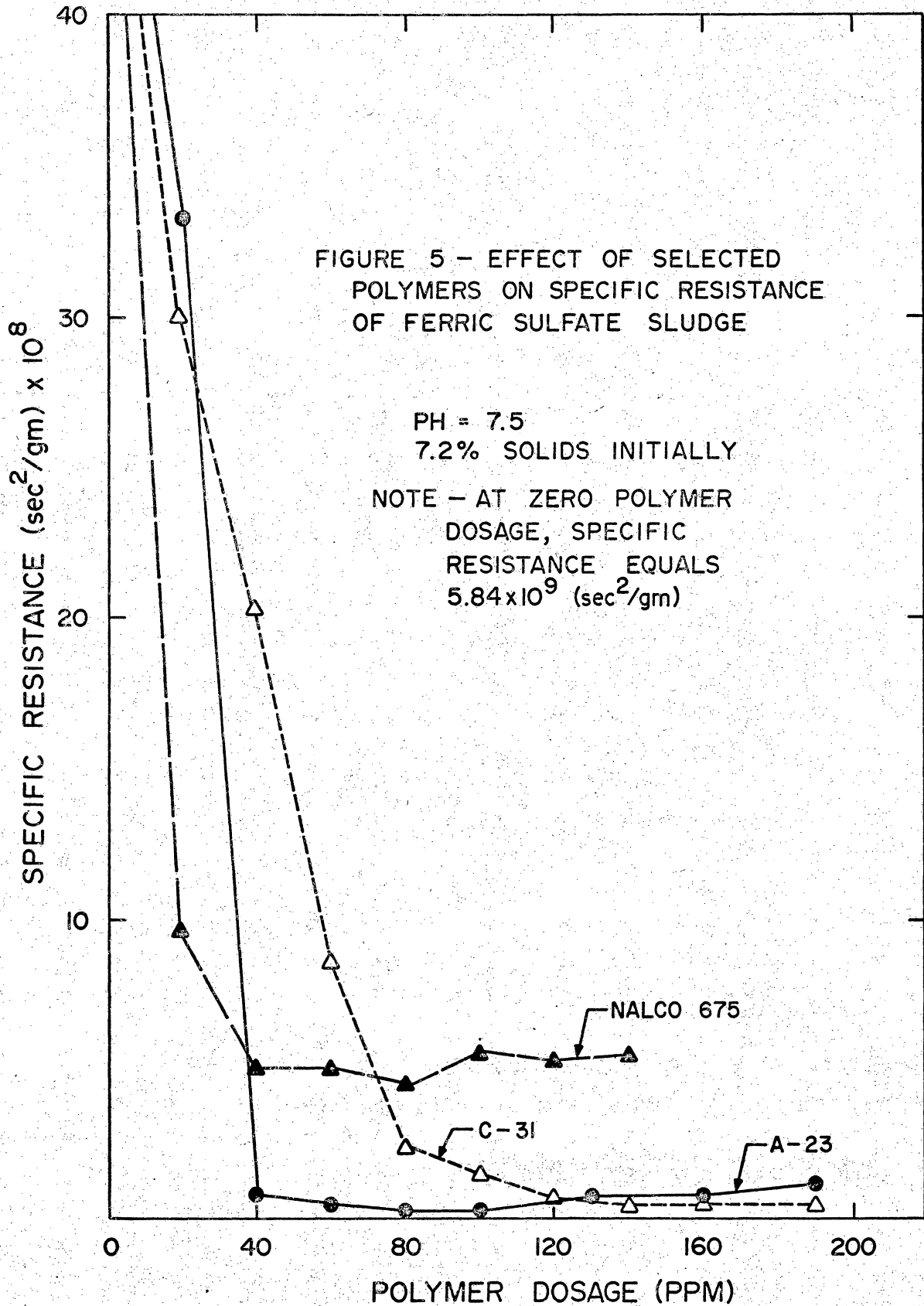Figure 3.

Figure 3 indicates that polyelectrolytes C-31, A-23 and Nalco
675 all did an excellent job of conditioning the ferric sulfate
sludge. Although N-17 also reduced the specific resistance of the
sludge, its results are far from being comparable to those of the
other polyelectrolytes. The optimum polyelectrolyte dosage for
C-31, A-23, Nalco 675 and N-17 occurred at 80 ppm, 60 ppm, 60 ppm
and 60 ppm respectively. At their optimum dosages C-31, A-23,
Nalco 675 and N-17 reduced the specific resistance of the sludge
from 5×10^9 (sec^2/gm) initially to 7.5×10^7, 4.5×10^7, 1.35×10^8
and 6.1×10^8 (sec^2/gm) respectively. A-23 and Nalco 675 exhibited
a greater effect on the specific resistance of the sludge at lower
polyelectrolyte dosages of 20 and 40 ppm than did the remaining
polyelectrolytes. All of the polyelectrolytes tended to increase
the specific resistance of the sludge at dosages above their optimum.
The increase in specific resistance caused by polyelectrolyte dosages
above optimum was most pronounced in N-17, while C-31, A-23 and
Nalco 675 all exhibited small increases. Sludge conditioned by
polyelectrolytes C-31, N-17 and Nalco 675 resulted in a finely divided
floc structure while sludge conditioned by A-23 exhibited a floc
structure composed of large lumps of conditioned sludge. Supernatant
from sludge conditioned with C-31 was extremely clear. On the other
hand N-17, A-23 and Nalco 675 yielded supernatant with varying degrees

FIGURE 3 – EFFECT OF SELECTED POLYMERS ON SPECIFIC RESISTANCE OF FERRIC SULFATE SLUDGE
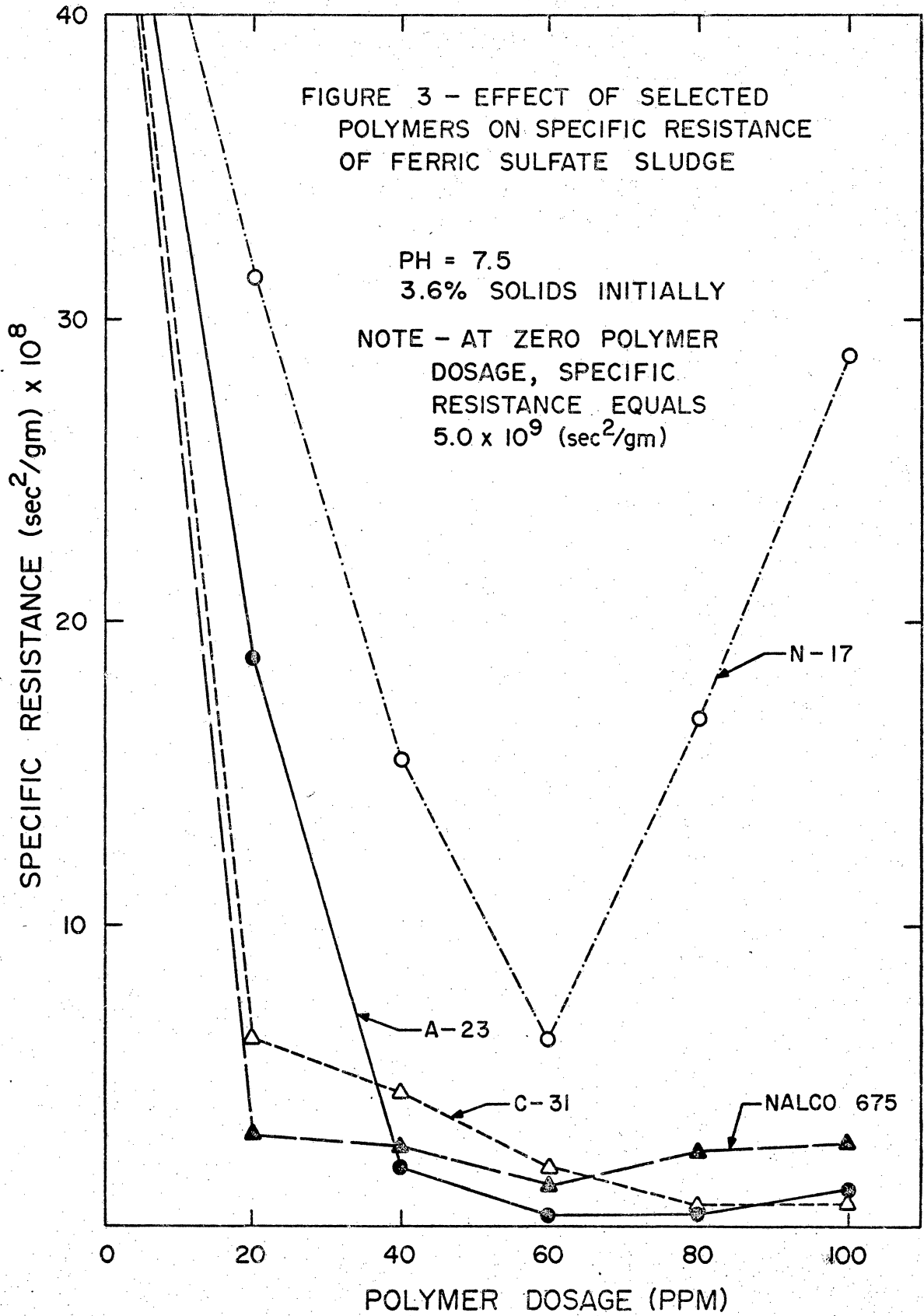
of turbidity.

Tests were then run with different sludge solids contents in order to determine the effect of solids on the specific resistance and the optimum dosage of polyelectrolyte required for conditioning the sludge. Solids contents of 1.8 per cent and 7.2 per cent were utilized at a system pH of 7.5. Only the three best polyelectrolytes, C-31, A-23 and Nalco 675, as determined in the tests with 3.6 per cent solids, were used in the variable solids content tests. Figure 4 shows the results of the 1.8 per cent solids tests, while Figure 5 shows the results of the 7.2 per cent solids tests. The results show that specific resistance is affected by the solids content of the sludge. At 7.2 per cent colids the unconditioned sludge has a specific resistance of 5.84 X 10^9 (sec^2/gm) while the 3.6 per cent solids sludge had a value of 5.00 X 10^9 (sec^2/gm). When the solids content was dropped to 1.8 per cent the specific resistance of the unconditioned sludge dropped to 3.4 X 10^9 (sec^2/gm). The optimum polyelectrolyte dosage was also affected by the initial solids content of the sludge. C-31 when tested at the different solids contents of 1.8, 3.6 and 7.2 per cent gave optimum polyelectrolyte dosages of 40, 80 and 140 ppm respectively. Optimum polyelectrolyte dosages of A-23 and Nalco 675 were also affected by the different solids contents. At solids contents of 1.8, 3.6 and 7.2 per cent, A-23 had optimum dosages of 20, 60 and 100 ppm respectively, while those of Nalco 675 were 40, 60, and 80 ppm respectively. Thus as the solids content of the sludge increased so did the optimum

FIGURE 4 — EFFECT OF SELECTED
POLYMERS ON SPECIFIC RESISTANCE
OF FERRIC SULFATE SLUDGE

PH = 7.5
1.8% SOLIDS INITIALLY

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FIGURE 5 – EFFECT OF SELECTED POLYMERS ON SPECIFIC RESISTANCE OF FERRIC SULFATE SLUDGE

PH = 7.5
7.2% SOLIDS INITIALLY

NOTE – AT ZERO POLYMER DOSAGE, SPECIFIC RESISTANCE EQUALS 5.84×10^9 (sec^2/gm)

dosages of all the polyelectrolytes. The results of the different

solids content tests also indicated that at optimum dosages, C-31

and A-23 did a more effective job than Nalco 675 in reducing the

specific resistance of the sludge.

Effect of System pH on the Specific Resistance of

Polyelectrolyte Conditioned Ferric Sulfate Sludge

Sludge containing 3.6 per cent solids was used throughout this

experiment. The polyelectrolyte dosages of N-17, C-31, A-23 and

Nalco 675 were the optimum ones determined for 3.6 per cent solids

at a pH of 7.5. (See Figure 3) Figure 6 shows the effects on speci-

fic resistance caused by varying the system pH. For polyelectro-

lytes N-17, A-23 and Nalco 675, tests were run at pH levels of 4.0,

6.0, 7.5 and 10. C-31, on the other hand, was run at all of the

above listed pH levels and also at a pH of 2.0. Results indicated

that the specific resistance of polyelectrolyte conditioned sludge

is very much affected by system pH. Polyelectrolytes C-31 and A-23

showed a maximum reduction in specific resistance at a pH of 7.5.

As the sludge became more basic both of the polyelectrolytes showed

a marked increase in specific resistance. A similar, but much less

drastic, increase was also noted for these polyelectrolytes as the

solution became more acidic. Results showed that Nalco 675 works

best at a slightly acidic pH of 6.0. Nalco 675 exhibited a slight

increase in specific resistance as the sludge became more acidic,

while at a more basic condition it showed the same drastic increase

in specific resistance that was noted in samples conditioned with

FIGURE 6 — EFFECT OF PH ON SPECIFIC RESISTANCE OF POLYMER CONDITIONED FERRIC SULFATE SLUDGE
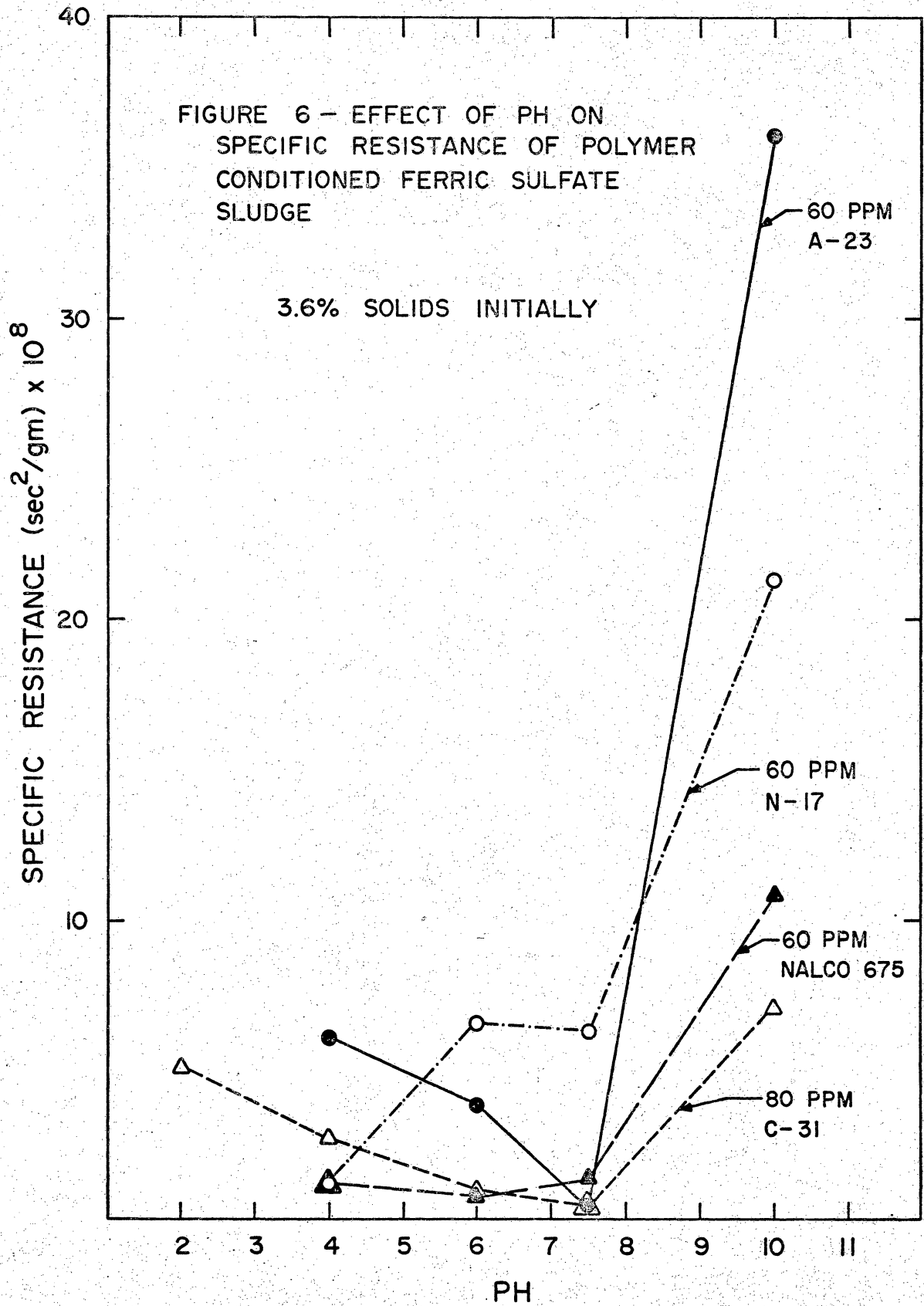
C-31 and A-23. N-17 gave an optimum reduction in specific resis-

tance at a pH of 4.0. In the pH range between 6.0 and 7.5 the

specific resistance of the N-17 conditioned sludge remained fairly

constant, but there was a large increase in specific resistance at

a pH of 10. When the sludge samples were reduced to a pH of 4.0

or 2.0 a metallic sheen developed on the surface of the sample and

a hydrogen sulfide odor was detected.

Effect of Polyelectrolytes on the Zeta Potential
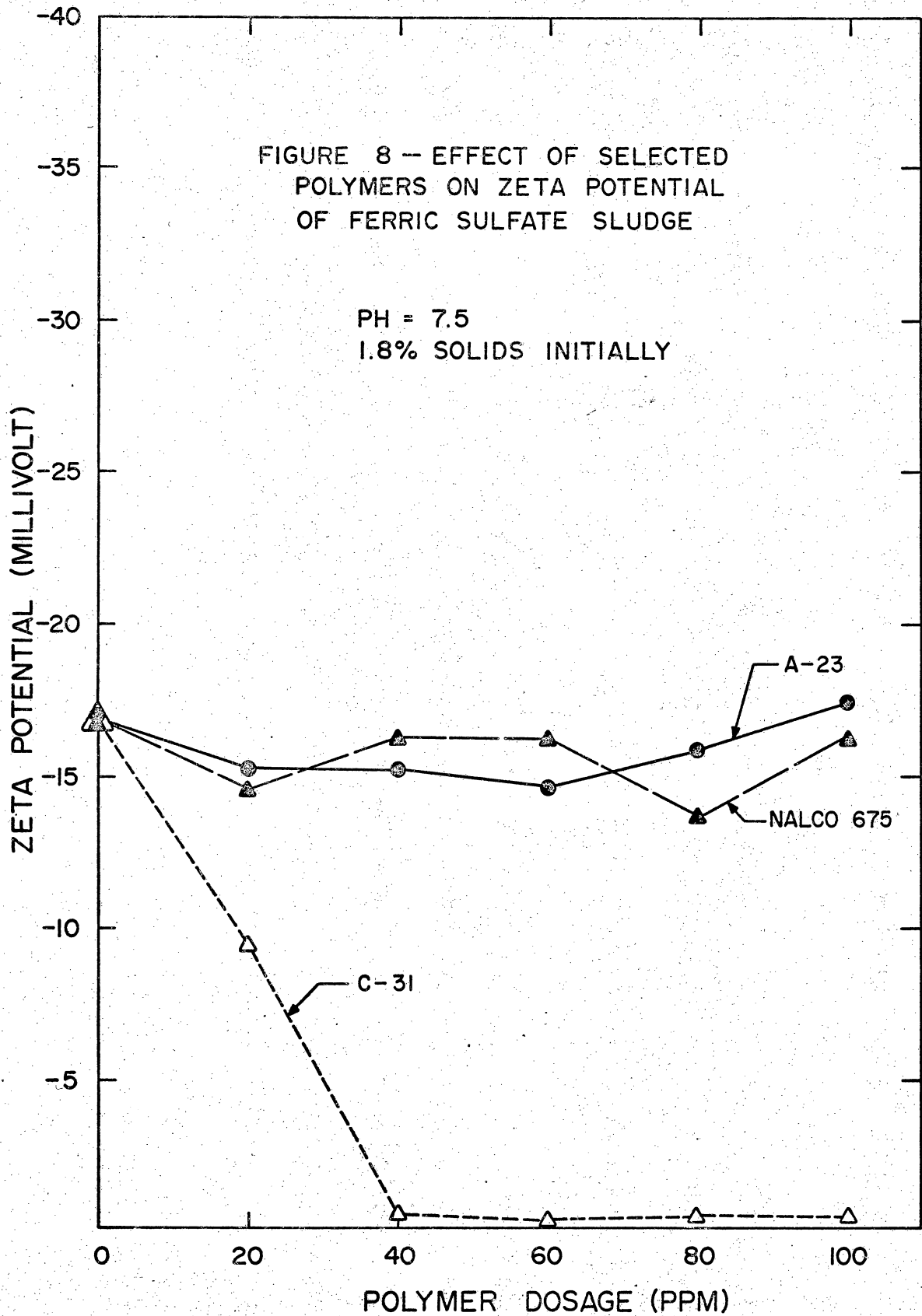### of Ferric Sulfate Sludge

Zeta potential determinations were run on the supernatant from

all 3.6 per cent solids sludge samples conditioned with polyelec-

trolytes N-17, A-23, C-31 and Nalco 675. The pH of the sludge was

7.5 while its zeta potential was -15 mv. The variance of zeta poten-

tial with polymer dosage for 3.6 per cent solids is shown in Figure 7.

As the dosages of N-17 and A-23 increased, the zeta potential also

increased in an electronegative direction. The zeta potential went

from -15 mv at zero dosage of N-17 and A-23 to -24 mv and -30 mv

respectively at a dosage of 100 ppm. Different dosages of Nalco 675

obviously had little effect on the zeta potential of the sludge. An

almost constant zeta potential is shown in Figure 7 for Nalco 675.

For N-17, A-23, and Nalco 675 the zeta potential did not reach a

peak in Figure 7 at the point of optimum polymer dosage found in

Figure 3. Increasing dosages of C-31 changed the zeta potential in

an electropositive direction until at 80 ppm a value of -.5 mv was

reached. This depression in the zeta potential at 80 ppm corres-

FIGURE 7 — EFFECT OF SELECTED POLYMERS ON ZETA POTENTIAL OF FERRIC SULFATE SLUDGE
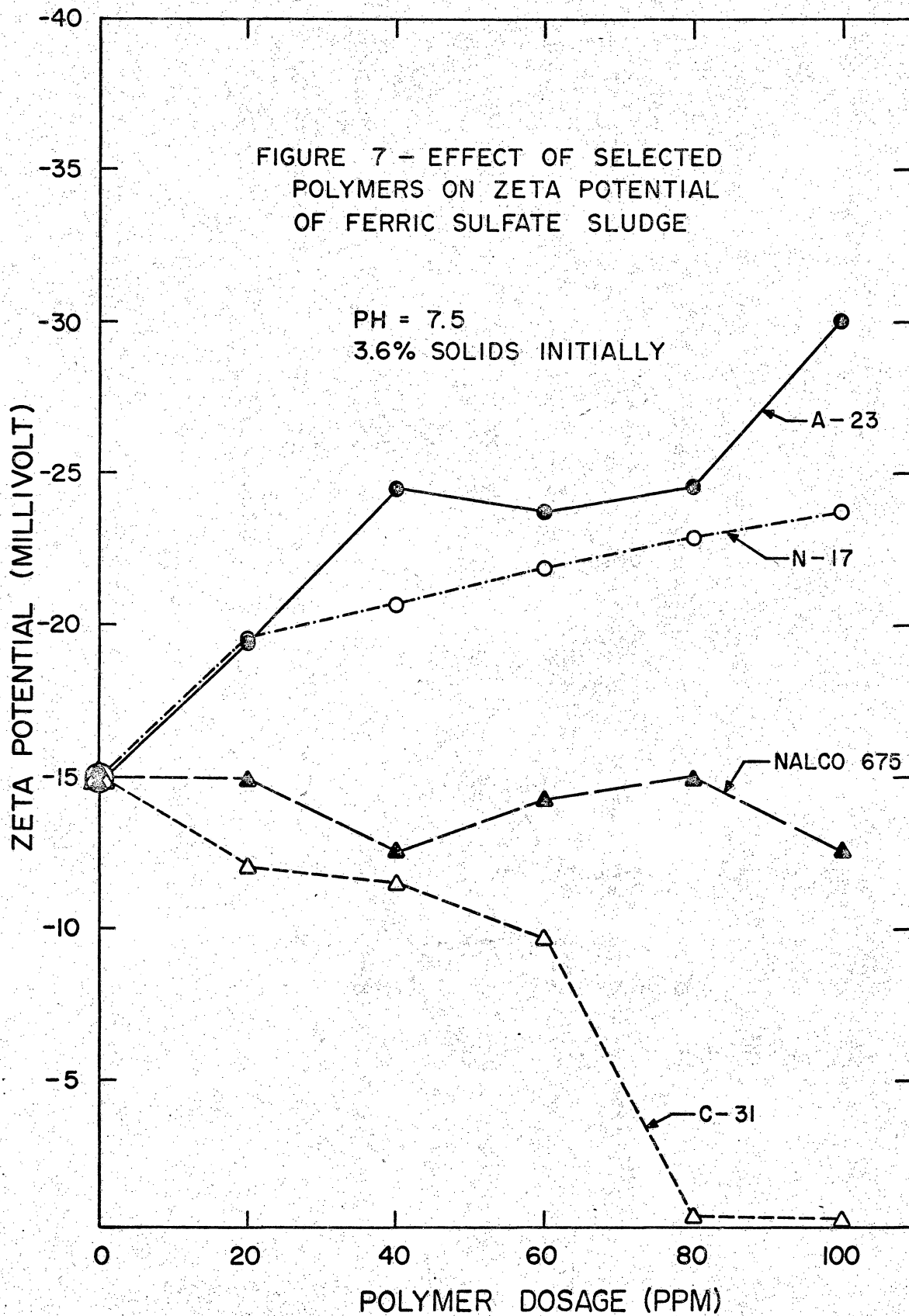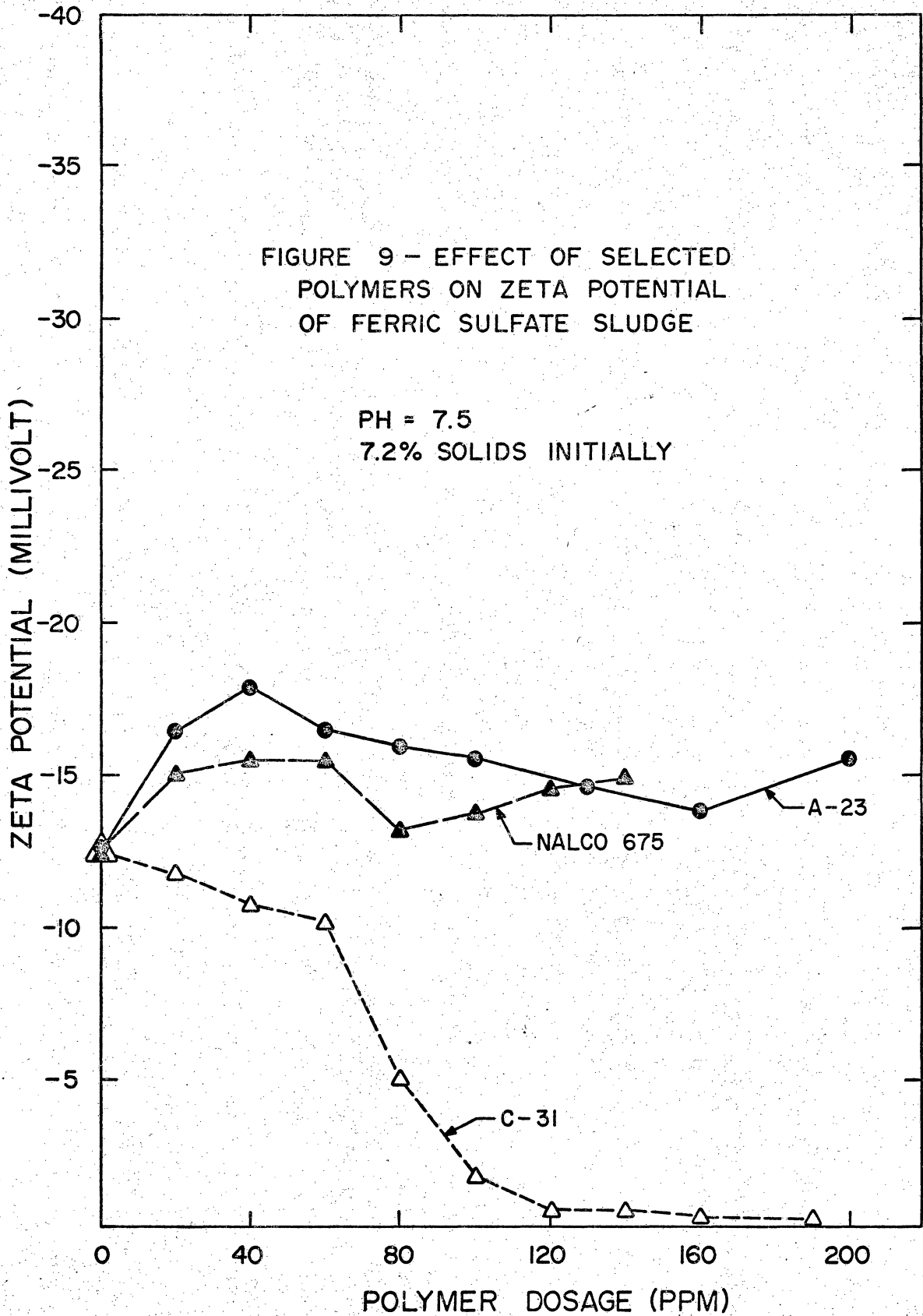
ponded to the optimum polyelectrolyte dosage shown in Figure 3 for C-31.

Zeta potential determinations were also run on supernatant from sludges of 1.8 and 7.2 per cent solids content that had been conditioned with varying dosages of A-23, Nalco 675 and C-31. The zeta potential of the 1.8 per cent solids, unconditioned sludge was -17 mv, and its pH was 7.5. The results of the determinations for the 1.8 per cent solids sludge are shown in Figure 8. A-23 and Nalco 675 had very little effect on the zeta potential of the sludge. The zeta potential remained essentially constant for dosages of A-23 and Nalco 675 ranging from 0 to 100 ppm. C-31 on the other hand did affect the zeta potential of the sludge. A change from -17 mv at zero dosage of C-31 to a -0.5 mv at a dosage of 40 ppm was noted. From 40 to 100 ppm the zeta potential remained a constant -0.5 mv. This depression at 40 ppm of C-31 corresponded to the optimum polyelectrolyte dosage shown in Figure 4 for C-31 at 1.8 per cent solids.

Figure 9 shows the results of the zeta potential determinations on supernatant from 7.2 per cent solids conditioned sludge. The pH of the system was 7.5. An unconditioned sample of the sludge resulted in a zeta potential determination of -12.5 mv. At dosages of 20 and 40 ppm the polyelectrolytes A-23 and Nalco 675 caused an electronegative increase in the zeta potential. As the dosages of these polyelectrolytes increased the zeta potential varied between -16 mv and -13 mv for both of them. C-31 again caused an electropositive change in the zeta potential that resulted in a value of

FIGURE 8 — EFFECT OF SELECTED
POLYMERS ON ZETA POTENTIAL
OF FERRIC SULFATE SLUDGE

PH = 7.5
1.8% SOLIDS INITIALLY

FIGURE 9 — EFFECT OF SELECTED
POLYMERS ON ZETA POTENTIAL
OF FERRIC SULFATE SLUDGE

PH = 7.5
7.2% SOLIDS INITIALLY

-0.7 mv at a dosage of 120 ppm. From 120 ppm to 190 ppm the zeta

potential remained fairly constant in the range between -0.7 mv and

-0.3 mv. The depression in the graph for C-31 in Figure 9 at a

dosage of 120 ppm corresponded to the optimum polyelectrolyte dosage

of C-31 for 7.2 per cent solids sludge.(See Figure 5)

Thus dosages of polyelectrolytes A-23 and Nalco 675 caused the

zeta potential to become more electronegative or to remain relatively

constant depending upon the initial solids content of the sludge.

On the other hand, dosages of C-31 caused an electropositive shift

in the zeta potential. This electropositive shift usually reached

a value of -1 mv at the polyelectrolyte dosage that was determined

to be optimum for the solids content of the sludge being considered.

(See Figures 3, 4, 5)

Effect of pH on the Zeta Potential of
Polyelectrolyte Conditioned Ferric Sulfate Sludge

Tests were run on a 3.6 per cent solids content sludge. The

sludge was conditioned with the optimum polyelectrolyte dosages

determined for 3.6 per cent solids.(See Figure 3) A-23, N-17 and

Nalco 675 were tested at pH levels of 4.0, 6.0, 7.5 and 10. C-31

was tested at all of these levels and also at a pH of 2.0. Results

of the zeta potential determinations are shown in Figure 10. pH

affected the zeta potential of all polyelectrolyte conditioned

sludges. At a pH of 7.5, N-17, A-23 and Nalco 675 reached peak zeta

potentials of -22 mv, -24 mv and -14 mv respectively. At all other

pH levels these three polyelectrolytes exhibited zeta potentials in

FIGURE 10 – EFFECT OF PH ON ZETA POTENTIAL OF POLYMER CONDITIONED FERRIC SULFATE SLUDGE
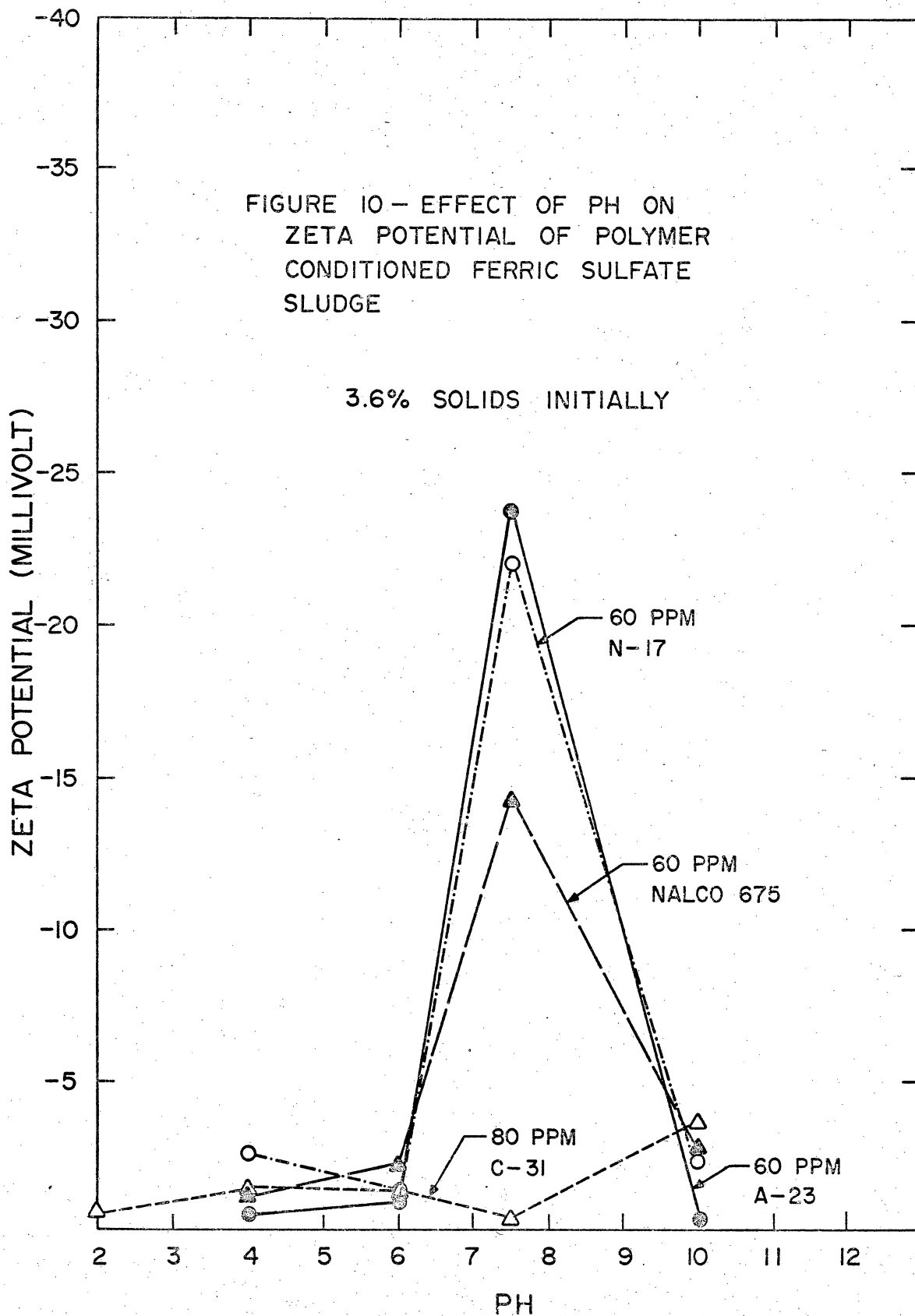
the range between -1 and -3 mv. By referring to Figure 6, it can
easily be seen that for A-23 and Nalco 675 a pH of 7.5 also gave
the best reduction in specific resistance. But on the other hand,
N-17 caused an optimum reduction in specific resistance at a pH of
4.0 while its zeta potential peaked at a pH of 7.5. C-31 dipped
to a low zeta potential value of -0.4 mv at a pH of 7.5. As the
sludge became more acidic the zeta potential for C-31 became slightly
more electronegative with values in the range between -1 mv and -2
mv. At a pH of 10 the zeta potential for C-31 increased electro-
negatively to a value of -4.0 mv. Figure 6 shows that the optimum
pH for C-31 to effectively condition sludge is 7.5, which is the
same pH at which the zeta potential dips to its most electroposi-
tive value.(See Figure 10)

Effect of Polyelectrolytes on Sand Bed Drying
of Ferric Sulfate Sludge

Sand bed studies were run using a 3.6 per cent solids content
sludge at a system pH of 7.5. Optimum polyelectrolyte dosages of
A-23, C-31 and Nalco 675, as determined for 3.6 per cent solids,
were used in the test.(See Figure 3) Three sand beds had condi-
tioned sludges applied to them, while one bed had an unconditioned
sludge applied to it. Cake moisture was determined by the method
previously described for gravity drainage and by coring during air
drying. The results of gravity drainage are shown in Figure 11. It
should be noted that the results shown have been corrected for eva-
poration in the manner previously described. The unconditioned

FIGURE 11 – BENCH SCALE
SAND BED STUDIES,
GRAVITY DRAINAGE
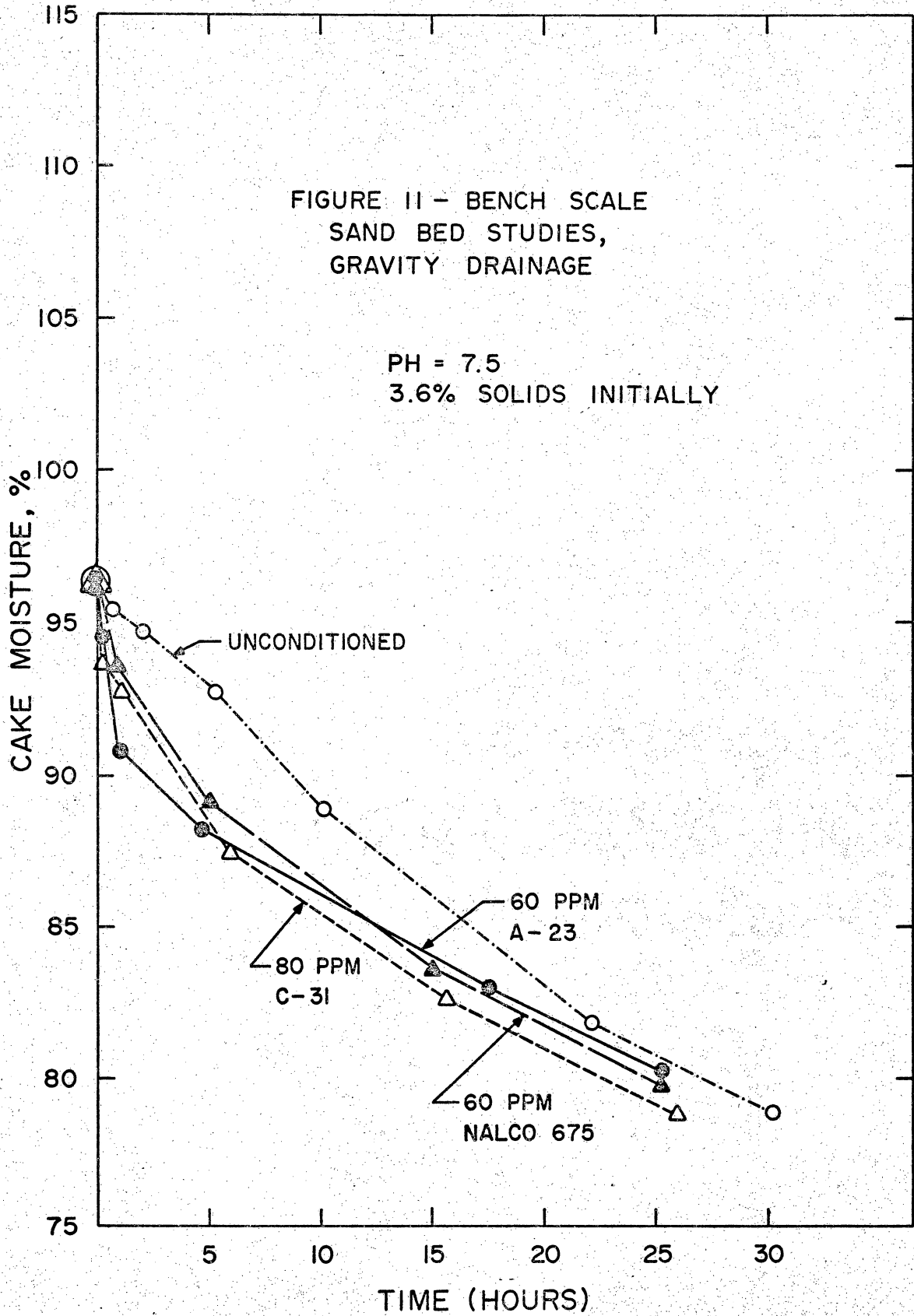
sludge did not dewater as rapidly as the polyelectrolyte conditioned

sludges. Gravity drainage was completed for the unconditioned sam-

ple in 30 hours with a resultant cake moisture of 88.8 per cent. No

cracks developed in the unconditioned sample during this time. When

applied to the bed the unconditioned sample settled, leaving a tur-

bid supernatant on top of the sludge. This supernatant then had to

filter through the sludge and the bed medium before it could be

recorded as drainage water. The sample that was conditioned with

A-23 was very lumpy when applied to the bed. It dewatered very

rapidly initially and large cracks that extended to the sand surface

developed in the sample within 10 minutes. The rate of gravity

drainage of A-23 decreased very rapidly after the first several hours.

A-23 completed its gravity drainage in 25 hours and with a final

cake moisture of 80.2 per cent. Nalco 675 and C-31 had gravity

drainage rates that were very similar. The Nalco 675 sample was

slightly lumpy after conditioning, while C-31 was almost completely

void of lumps. Sludge conditioned with Nalco 675 or C-31 dewatered

rapidly for the first several hours after which its rate of de-

watering decreased. Gravity drainage for Nalco 675 and C-31 ended

at 25 and 26 hours respectively. The final cake moisture of the

Nalco 675 sample was 89.8 per cent while that of C-31 was 88.7 per

cent. Cracks did not develop in either the Nalco 675 or the C-31

samples during gravity drainage. Both Nalco 675 and C-31 dewatered

in a fashion similar to that explained for the unconditioned sludge.

Solids did not penetrate into the bed medium on any of the condi-

tioned samples and penetration was only to one-fourth inch with the unconditioned sample.

Figure 12 shows the result of air drying of the sludge samples. The time axis was continued from the gravity drainage graph.(see Figure 11) When air drying started the cake moisture of the unconditioned sludge sample had become less than that of the A-23 and Nalco 675 samples. At this time C-31 still had a cake moisture content less than that of the unconditioned sample. Air drying continued for 20 days. During the second day of air drying or the third day of the total test, cracks developed in the Nalco 675 and the C-31 samples. These cracks extended to the interface between the sludge and the sand. The unconditioned sample did not develop any cracks until the 19th day of the test. Cake moisture results show that A-23 was the best sludge conditioner with a final value of 70 per cent. Nalco 675 and C-31 had final cake moisture values of 72.5 and 73.7 per cent respectively. The unconditioned sample reached a final cake moisture of 74.5 per cent at the end of 21 days. A-23 was the sample most easily removed from the bed.

FIGURE 12 — BENCH SCALE
SAND BED STUDIES,
AIR DRYING

PH = 7.5
3.6% SOLIDS INITIALLY
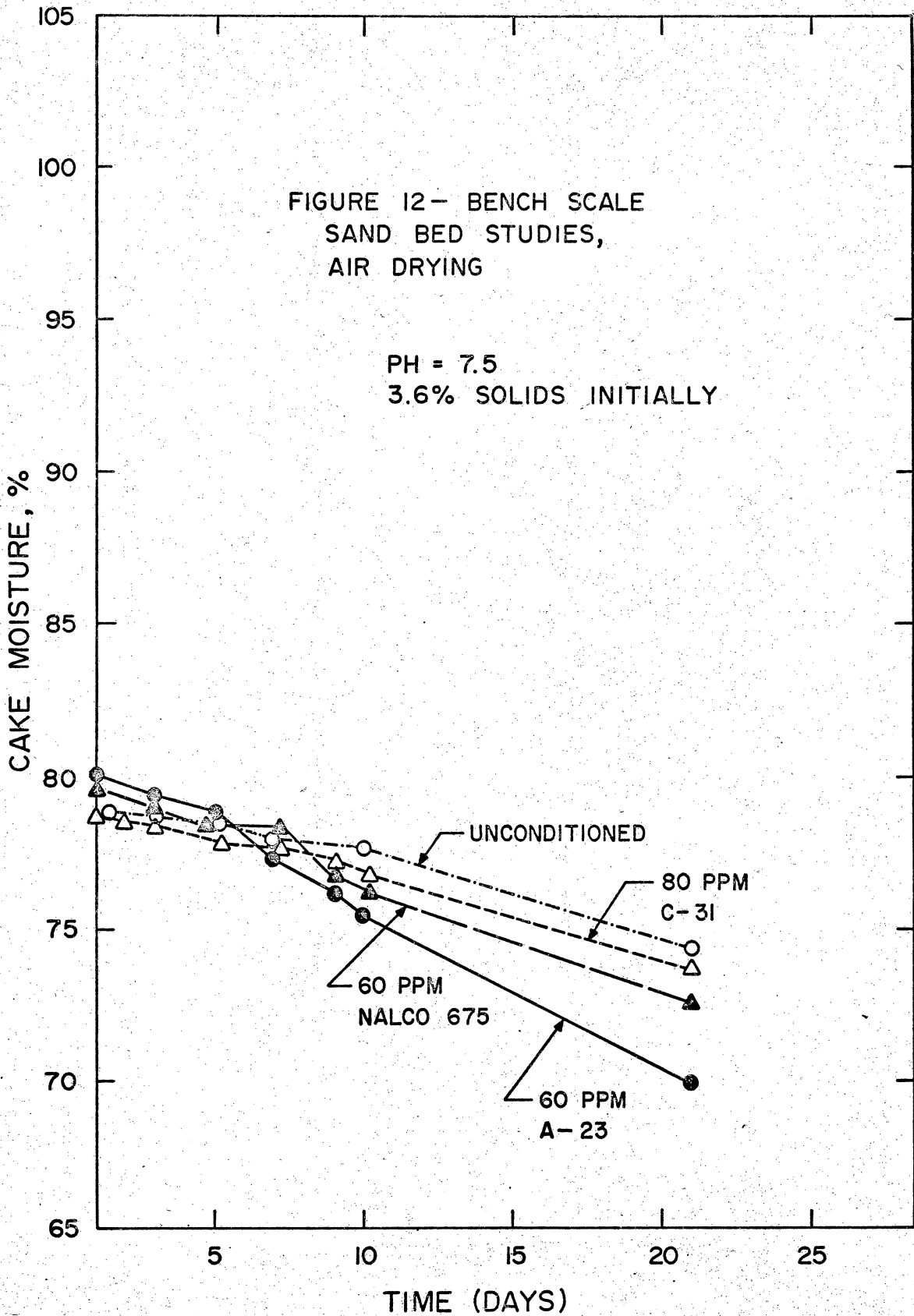
V. DISCUSSION OF RESULTS

The purpose of this investigation was to furnish technical information concerning polyelectrolyte conditioning of ferric sulfate sludge. The results of this investigation are a significant step toward understanding more about conditioning of this type of water plant sludge. An analysis of the important results obtained in the investigation follows.

Sludge Characterization

Proper sludge characterization is of great importance in the discussion of the results of this investigation. The adaptability of the results to other water treatment plant sludges hinges on how well the sludge used in this investigation was characterized.

The sludge had a pH that was slightly more acidic than the treated water from the plant. This slight reduction in pH can be accounted for by decomposition by microorganisms of some of the organic matter present in the sludge. The solids content of the sludge being pumped to the lagoon after the draining of the basin was found to be 3.6 per cent. Gates and McDermott recorded a somewhat higher value of 4.1 per cent solids for alum sludge that was cleaned from a sedimentation basin in the same manner as the ferric sulfate sludge used in this investigation.(23) Bugg recorded COD values for alum sludge in the range between 1,000 and 1,300 mg/l.(19) The COD values found for ferric sulfate sludge in this investigation were much higher.(See Table V) The one factor which added most to the large difference in COD values was the fact

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that activated carbon was used in the Carvins Cove plant, while the
plant in Bugg's investigation did not use it. The fact that differ-
ent raw water sources and coagulant aids were used also affected the
COD values. Bugg found that approximately 15 per cent of the total
solids of the alum sludge used in his investigation was measured as
volatile solids.(19) Results for ferric sulfate sludge indicated
that 20 per cent of the total solids of the sludge was volatile.
This increase in volatile solids can be accounted for by the pre-
sence of activated carbon in the ferric sulfate sludge. Gates and
McDermott noted in their investigation of alum sludge that activated
carbon increased the volatile solids content of the sludge by as
much as 30 per cent.(23)

The specific resistance of ferric sulfate sludge containing
3.6 per cent solids was 5.0 X 10^9 sec^2/gm. This value is consider-
ably higher than the values associated with alum sludge. For exam-
ple, Gates and McDermott recorded a specific resistance value for
alum sludge with 4.1 per cent solids of 2.07 X 10^9 sec^2/gm.(23)
Therefore unconditioned ferric sulfate sludge did not exhibit as
good filterability as unconditioned alum sludge.

Polyelectrolyte Conditioning of Ferric

Sulfate Sludge

This investigation indicates that polyelectrolyte adsorption is
almost immediate. This result agrees with the conclusion by Black,
Birkner and Morgan that polyelectrolyte adsorption is 85 per cent
complete in 30 seconds.(20) The flash mix for two minutes at 100 rpm

used in this investigation was necessary to suspend the solid-poly-electrolyte mixture and to enhance contacts between the two phases. If the agitation exceeded two minutes the floc structure originally formed tended to break up, thus increasing the specific resistance of the sample. Bugg noted this same disintegration of the poly-electrolyte-particle floc structure with an increased time of agitation over two minutes. He concluded that the disintegration resulted from excess agitation that caused the floc to be broken up and the polyelectrolyte segments to curl back and become attached to themselves.(19) The same conclusion was drawn for the disintegration of the ferric sulfate floc noted in this investigation.

In this investigation cationic, anionic and nonionic polyelectrolytes improved the filterability of the ferric sulfate sludge. The effect of the polyelectrolytes on the sludge can best be explained by the coagulation-flocculation theory developed by La Mer. From the results plotted on Figure 3 it can be concluded that the anionic polyelectrolytes A-23 and Nalco 675 both reduced sludge specific resistance. The zeta potential results plotted on Figure 7 for the same two anionic polyelectrolytes, indicate that increased dosages of the polyelectrolytes caused the zeta potential to become more electronegative or to remain essentially constant. Thus the anionic polyelectrolytes conditioned the sludge by the mechanism of chemical bridging or flocculation described by La Mer.(12) Since there was essentially no reduction in the zeta potential, no charge neutralization occurred. Thus the mechanism involved must have been
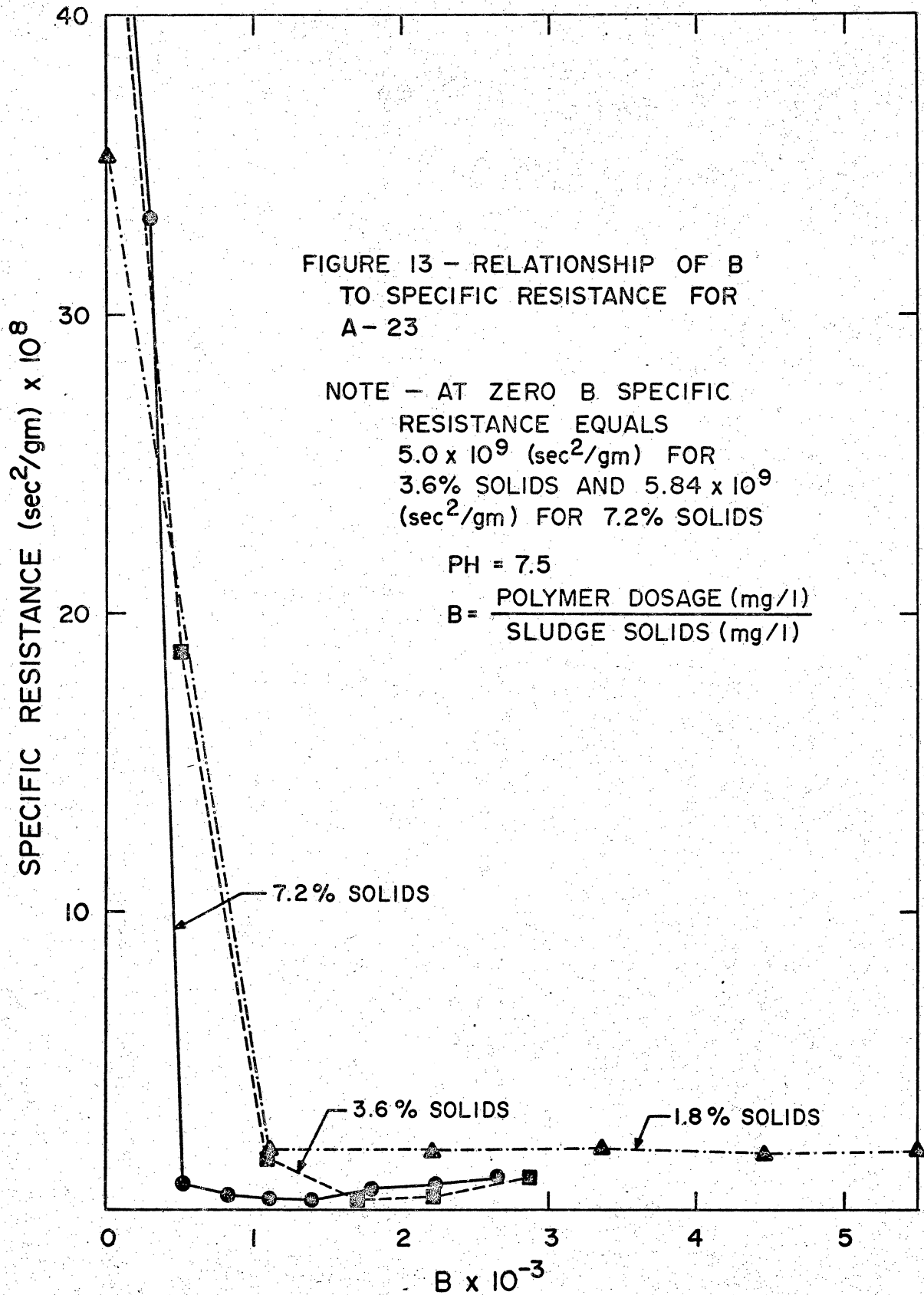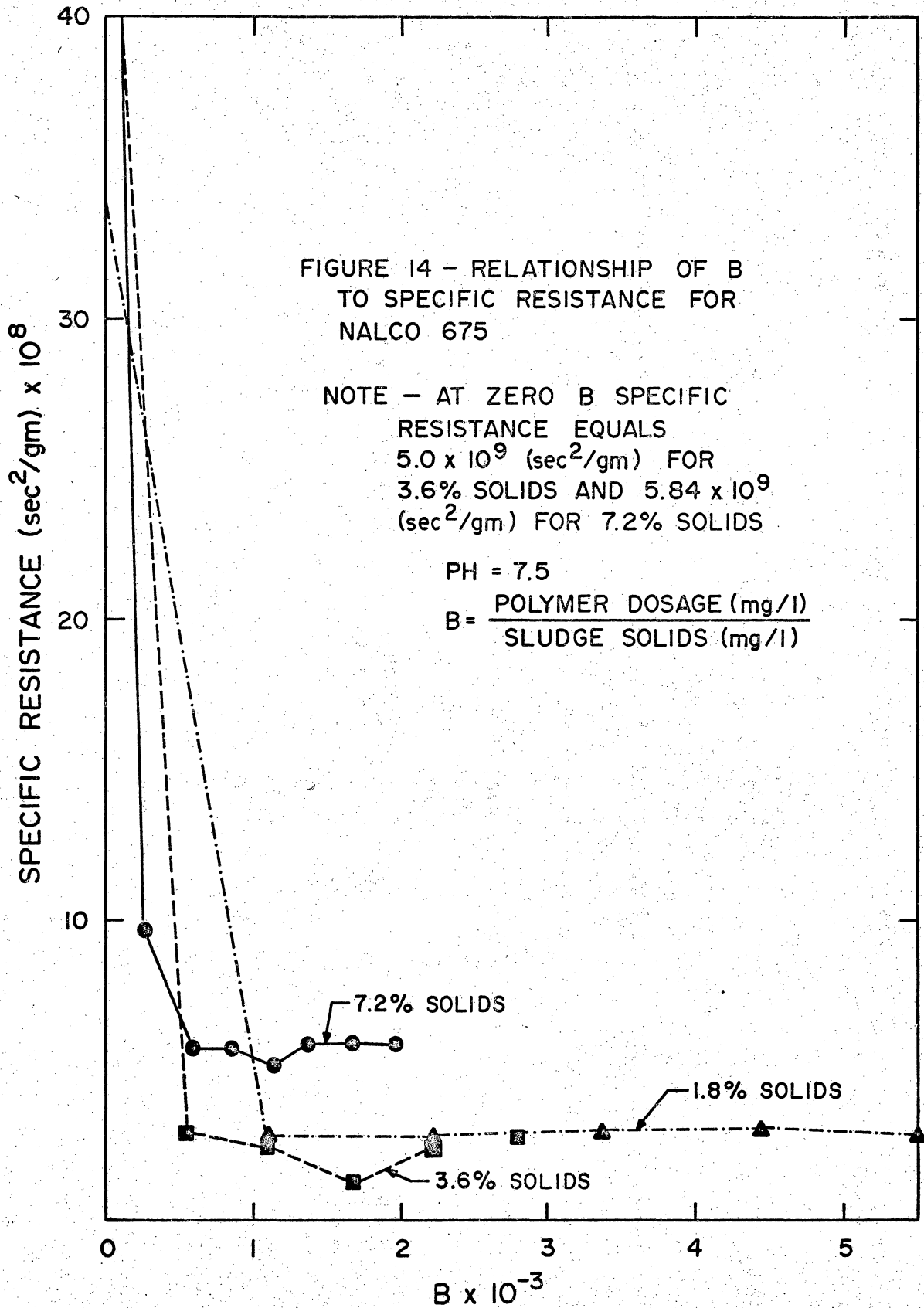
chemical bridging.

The results plotted on Figures 3 and 7 for the nonionic poly-electrolyte N-17 indicate that chemical bridging was the mechanism of sludge conditioning. With N-17 the zeta potential increased with increasing polyelectrolyte dosages. Thus no charge neutralization occurred. The results for cationic polyelectrolyte C-31 are also shown in Figures 3 and 7. C-31 decreased the specific resistance of the sludge considerably, while it also reduced the zeta potential in an electropositive direction to a value near zero. Thus C-31 caused considerable charge neutralization at dosages of 80 ppm and greater. At dosages less than 80 ppm it changed the zeta potential in an electropositive direction to only a slight extent yet it still re-duced the specific resistance in this dosage range. The optimum reduction in specific resistance occurred at 80 ppm, which was also the dosage at which the zeta potential almost reached zero. Thus a combined chemical bridging and charge neutralization or coagulation theory must be used to explain the mechanism of sludge conditioning by C-31. Results of conditioning by the polyelectrolytes at differ-ent sludge solids contents also verify the conditioning mechanisms described above.(See Figures 4, 5, 8 and 9)
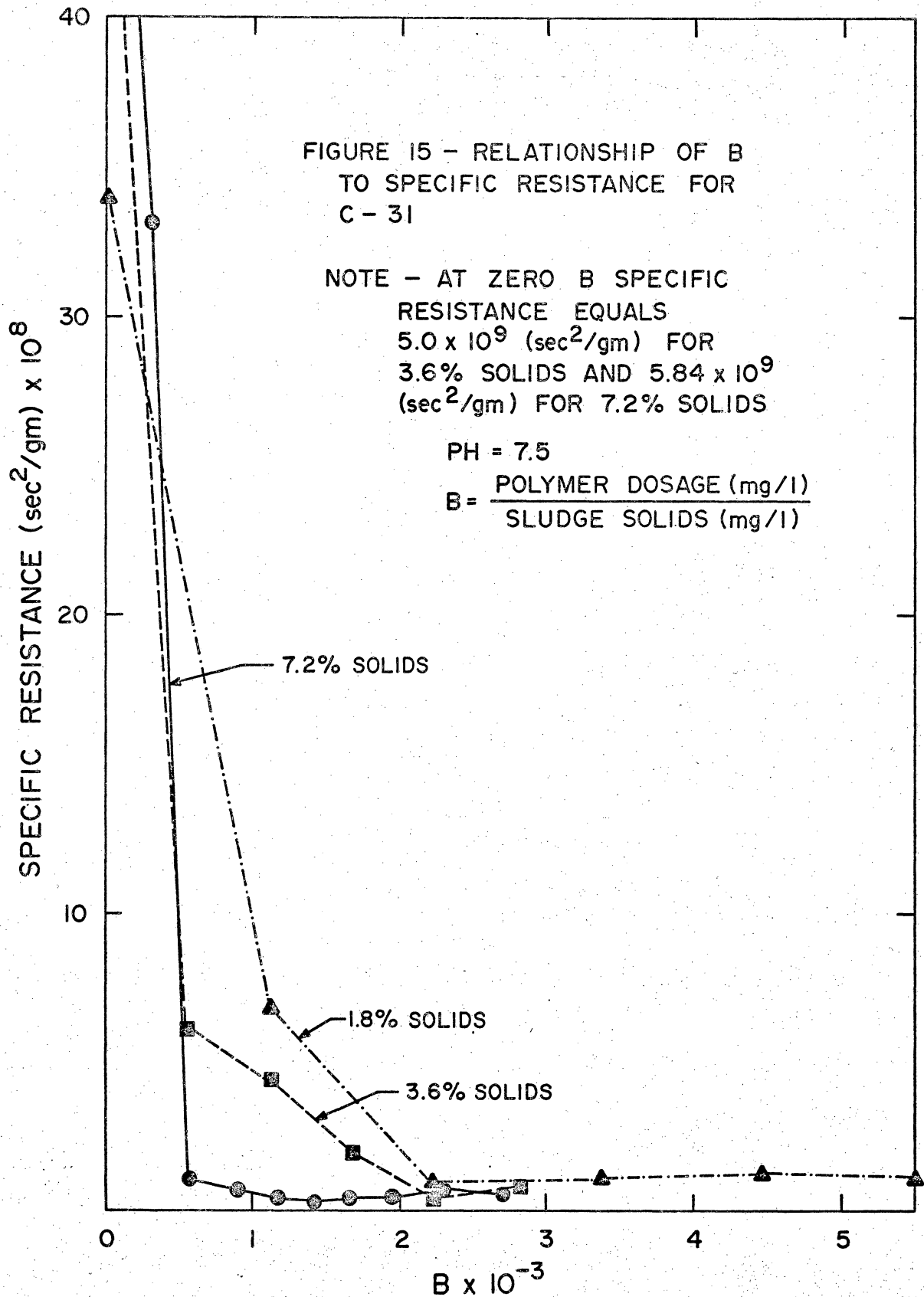
Sludge solids content played an important role in polyelectro-lyte conditioning. The results of this investigation indicate that sludge solids contents affect the optimum polyelectrolyte dosage or the dosage that gives the best reduction in specific resistance. For example, the optimum polyelectrolyte dosages of A-23 required

for sludge containing 1.8, 3.6 and 7.2 per cent solids were 20, 60

and 100 ppm respectively. This effect of increased optimum poly-

electrolyte dosage with increased sludge solids content was also

seen in the results of the other polyelectrolytes used in the inves-

tigation. (See Figures 3, 4 and 5) La Mer and Healy noted in their

chemical bridging theory that sludge solids content determined the

amount of polyelectrolyte required for the best destabilization.

They concluded that as the sludge solids content increased the num-

ber of adsorption sights available for the polyelectrolyte increased,

thus requiring a larger optimum polyelectrolyte dosage. (21) Their

conclusion was obviously verified in this investigation.

The effects of solids upon the optimum polyelectrolyte dosage

are further exemplified by the plots of specific resistance versus

the ratio B of polyelectrolyte dosage to sludge solids content.

Figures 13, 14 and 15 show the results of these plots for polyelec-

trolytes C-31, Nalco 675 and A-23. Although sludge solids content

affected the optimum polyelectrolyte dosage it can be shown by the

above figures that the B ratio that gave the maximum reduction in

specific resistance remained fairly constant for different sludge

solids contents. This indicates that there is one ratio of poly-

electrolyte dosage to sludge solids content for each polyelectrolyte

that gives maximum reduction in specific resistance. For example,

anionic polyelectrolytes A-23 and Nalco 675 gave the best reduction

in specific resistance when the B ratio was between 1.1×10^{-3} and

1.7×10^{-3}. (See Figures 14 and 15) The cationic polyelectrolyte

FIGURE 13 – RELATIONSHIP OF B
TO SPECIFIC RESISTANCE FOR
A – 23

NOTE – AT ZERO B SPECIFIC
RESISTANCE EQUALS
5.0×10^9 (sec^2/gm) FOR
3.6% SOLIDS AND 5.84×10^9
(sec^2/gm) FOR 7.2% SOLIDS

PH = 7.5

$$B = \frac{\text{POLYMER DOSAGE (mg/l)}}{\text{SLUDGE SOLIDS (mg/l)}}$$

FIGURE 14 – RELATIONSHIP OF B TO SPECIFIC RESISTANCE FOR NALCO 675

NOTE – AT ZERO B SPECIFIC RESISTANCE EQUALS 5.0×10^9 (sec^2/gm) FOR 3.6% SOLIDS AND 5.84×10^9 (sec^2/gm) FOR 7.2% SOLIDS

PH = 7.5

$$B = \frac{\text{POLYMER DOSAGE (mg/l)}}{\text{SLUDGE SOLIDS (mg/l)}}$$

FIGURE 15 – RELATIONSHIP OF B
TO SPECIFIC RESISTANCE FOR
C – 31

NOTE – AT ZERO B SPECIFIC
RESISTANCE EQUALS
5.0×10^9 (sec^2/gm) FOR
3.6% SOLIDS AND 5.84×10^9
(sec^2/gm) FOR 7.2% SOLIDS

PH = 7.5

$B = \dfrac{POLYMER\ DOSAGE\ (mg/l)}{SLUDGE\ SOLIDS\ (mg/l)}$

C-31 on the other hand exhibited a B value of 2.2 X 10^{-3} for maximum reduction in specific resistance. This indicates that cationic polyelectrolytes require a greater dosage per unit solids than anionic polyelectrolytes in order to obtain the maximum reduction in specific resistance. Since C-31 used a mechanism of chemical bridging and charge neutralization in conditioning, while A-23 and Nalco 675 used just chemical bridging, it stands to reason that a greater dosage of C-31 would be required per unit sludge solids to complete the conditioning mechanism. The B ratio could, with more testing, be developed into a very important parameter for polyelectrolyte conditioning.

From the results of this investigation it can be concluded that pH was of great importance in polyelectrolyte conditioning of ferric sulfate sludge.(See Figures 6 and 10) pH affects the polyelectrolyte and the surface of the particle, which in turn affects the specific resistance and the zeta potential of the conditioned sludge. The relationship between pH and the effects stated above is very complex. For example, a reduction in pH both alters the zeta potential of the unconditioned sludge and also changes the per cent hydrolysis of the polyelectrolyte when it is added to the unconditioned sludge. The results indicated that for anionic and cationic polyelectrolytes the optimum pH range for the maximum reduction in specific resistance was between 6.5 and 7.5. The polyelectrolyte and the unconditioned sludge were virtually unaltered by pH in this range. Zeta potential peaked for A-23 and Nalco 675 and dropped for C-31 in

this pH range, thus confirming the various conditioning mechanisms already proposed for each polyelectrolyte. At pH's above and below the 6.5 to 7.5 range, changes in the polyelectrolytes and the sludge particles competed with each other, and the net result was an increase in the specific resistance for cationic and anionic conditioned sludges. Nonionic polyelectrolyte N-17 had a maximum reduction in specific resistance in the pH range near 4.0 while its zeta potential peaked at a pH of 7.5. This result indicated that the polyelectrolyte and the sludge particles were altered in such a manner that they were more compatible for conditioning. The result was a decrease in the specific resistance of the conditioned sludge. It can be concluded that the effects of pH in sludge conditioning are quite complex.

Bench scale sand bed studies revealed that polyelectrolytes did enhance the dewaterability of the ferric sulfate sludge.(See Figures 11 and 12) Sludge conditioned with A-23 produced the cake with the best moisture content after twenty-one days. All the polyelectrolyte conditioned samples exhibited an open or porous floc structure, but the floc structure exhibited by A-23 was by far the best. The superb floc structure shown by A-23 can be attributed to the chemical properties of the polyelectrolyte along with the fact that the zeta potential at the optimum dosage was -25 mv. At this rather electronegative zeta potential repulsive forces existed between sludge particles which caused a porous floc structure to form. A-23 was easily removed from the bed due to the porous floc structure. Sam-

ples conditioned with C-31 and Nalco 675 gave more compact flocs as indicated by their more electropositive zeta potentials at optimum polyelectrolyte dosages.(See Figure 7) Although the floc structure of C-31 and Nalco 675 did dewater well during gravity drainage their structure was not porous enough to compete with A-23 during air drying. When conditioned sludge samples were applied to the beds it was noted that the chemical bridging mechanism prevented solids from penetrating into the top of the sand layer as they did in the unconditioned sludge sample. The fact that the two anionic polyelectrolytes produced different conditioning results can be accounted for by the difference in the chemical properties of molecular weight and per cent hydrolysis between the two polymers. Results indicate that specific resistance gave only a qualitative measure of the effect of polyelectrolytes on gravity dewatering and was not a quantitative indicator of the effectiveness of sand bed drying.

Cost figures for the polyelectrolytes used in the conditioning of ferric sulfate sludge are given in Table VI. The price data was obtained from the Purchasing Departments of Nalco Chemical and Dow Chemical. The costs were calculated from the rates for the smallest quantity obtainable from each company. The table indicates that the cost of polyelectrolytes used in conditioning was small when compared to the other capital outlays that might be encountered in finding a final method of sludge disposal.

TABLE VI

POLYELECTROLYTE COST DATA

POLYELECTROLYTE	OPTIMUM DOSAGE	COST PER 1000 GALLONS OF SLUDGE TREATED
Dow A-23	60 ppm	$1.30
Nalco 675	60 ppm	$0.95
Dow C-31	80 ppm	$1.66
Dow N-17	60 ppm	$1.38

VI. CONCLUSIONS

The results of this investigation dealing with the polyelectro-
lyte conditioning of ferric sulfate sludge support the following
conclusions:

1. All cationic, anionic and nonionic polyelectrolytes inves-
   tigated reduced the specific resistance of ferric sulfate
   sludge.

2. Specific resistance proved to be a qualitative measure of
   the effect of polyelectrolytes on gravity dewatering by
   sand bed drying of ferric sulfate sludge.

3. Polyelectrolyte adsorption was very rapid.

4. La Mer's flocculation or chemical bridging theory explains
   the mechanism involved in polyelectrolyte conditioning with
   anionic and nonionic polyelectrolytes. Cationic polyelec-
   trolyte conditioning is explained by La Mer's chemical bridg-
   ing theory with the added effect of charge neutralization
   being apparent.

5. pH affected the polyelectrolyte used in conditioning as well
   as the surface of the sludge particles and in turn affected
   the specific resistance and zeta potential of the conditioned
   sludge.

6. Sludge solids content affected the optimum polyelectrolyte
   dosage required for maximum reduction in specific resistance.
   The ratio of polymer dosage to sludge solids content giving
   maximum reduction in specific resistance remained fairly

constant for varying sludge solids contents.

7. Anionic polyelectrolytes produced the most porous floc structure which resulted in the best final cake moisture when applied to the sand beds.

8. Polyelectrolyte conditioning of ferric sulfate sludge was relatively inexpensive.

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POLYELECTROLYTE CONDITIONING

OF

FERRIC SULFATE SLUDGE

by

John Wade Olver

Abstract

Tests were run on samples of ferric sulfate sludge collected
from the sedimentation basins of a water treatment plant during
basin cleaning operations. The purpose of the testing was to deter-
mine if cationic, anionic and nonionic polyelectrolytes could suc-
cessfully condition the sludge to improve its dewaterability. In
addition the parameters which affected the conditioning mechanism
were investigated. Tests that were run during the investigation
included specific resistance, COD, total and volatile solids, zeta
potential and pH. Polyelectrolyte conditioned and unconditioned
sludge samples were applied to bench scale sand beds to determine
the effect of conditioning on the dewatering rate of the sludge.

Results indicated that all types of polyelectrolytes used
reduced the specific resistance of the sludge. However, specific
resistance was only a qualitative measure of the effect of poly-
electrolytes on gravity dewatering of the sludge. Anionic and
nonionic polyelectrolytes exhibited chemical bridging as the mechan-
ism of conditioning while cationic polyelectrolytes conditioned by

both chemical bridging and charge neutralization. Both pH and sludge

solids content were found to affect the conditioning process. The

sand bed studies indicated that sludge conditioned with anionic

polyelectrolytes produced a more porous floc structure that dewater-

ed to a cake that was easily removed from the bed. Cost data for

polyelectrolytes indicated that conditioning of the sludge by this

method was very economical.