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JULY 1988

RESEARCHING AND SPREADING A NEW TECHNIQUE OF PARTIAL DESALINATION

BY ION EXCHANGE USING CARBON DIOXIDE

AS REGENERANT

DP/CPR/86/023/11-02

REPUBLIC OF CHINA

CONSULTANT'S REPORT *

Prepared for the Government of China

by the United Nations Industrial Development Organization

Acting as executing agency for the United Nations Development Programme

Based on the work of Prof. Dennis Clifford

Director of Environmental Engineering

University of Houston

Houston, Texas 77004

Backstopping Officer: R.O. Williams, Chemical Undustries Branch

United Nations Industrial Development Organization

Vienna

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CONSULTANT'S REPORT

by

Professor Dennis Clifford
Director of Environmental Engineering
University of Houston
Houston, Texas 77004

for

United Nations Industrial Development Organization

Post: Expert in Water Treatment and Desalination,
DP/CPR/86/023/11-02/J13424

Introduction

During the two week period of 13 June 1988 through 26 June 1988 I did library research and prepared lectures on the subject of "The Removal of Colloidal Silica from Water". During the two week period beginning 27 June 1988 and ending 5 July 1988 I traveled from the U.S.A. to Beijing, China and then to Shandong Province to deliver lectures and act as a consultant on colloidal silica removal at the Second Fertilizer Factory of the Qilu Petrochemical Industry Corporation in Xindian, Zibo. Professor Yun Guichun of the Tsinghua University Institute of Nuclear Science and Technology acted as a liason between the Qilu Company and me, made my travel arrangements, and accompanied me on the visit to the Second Fertilizer Factory in Shandong Province. In addition to preparing and delivering lectures on colloidal silica, I assembled a three-ring binder containing more than 300 pages of articles on ion exchange and colloidal silica. I presented this binder to Professor Yun after a copy was made for use at the Qilu Second Fertilizer Factory. Additionally, I left copies of the originals of my 48 lecture presentation slides with

Professor Yun and the Qilu Company. Copies are also contained in this report as Appendix B.

During the period of 6 July 1988 through 10 July 1988 I travelled back to Beijing and presented lectures at Tsinghua University on "Ion Exchange for Water and Wastewater Treatment," and acted as a consultant in water treatment. My lectures at Tsinghua University were delivered in the Department of Environmental Engineering. Prior to delivering my lectures, I presented Professor Yun with copies of about 25 of my research publications for use at Tsinghua University. Some of these papers and reports were used by Mr. Liu Xiaosha who acted as a very capable translator for my lectures. Finally, I spent one day visiting the Institute of Nuclear Energy and Technology of the University.

Professor Yun also acted as my liason with Tsinghua University, was present at all my lectures, and accompanied me on my visits to the Environmental Engineering and Nuclear Energy Technology Laboratories of the University. I take this opportunity to acknowledge the excellent hospitality I received from both the Qilu Petrochemical Industry Corp. and Tsinghua University. I am particularly grateful to Professor Yun Guichun of Tsinghua University and to Mr. Zhao Motang, Deputy General Engineer of the Qilu Petrochemical Company Second Fertilizer Factory, for seeing to it that I was well taken care of while in China.

The Problem of Colloidal Silica at Qilu

The groundwater that is treated by ion exchange and used for boiler feedwater at the Second Fertilizer Factory contains 1-6 ppm colloidal silica that is not efficiently removed by the ion exchange process during certain times of the year. This leakage of colloidal silica into the treated boiler feedwater has led to high silica concentrations in the steam with subsequent fouling of the turbine blades.

On occasion, the high silica at Qilu has forced the factory to reduce the operating load, thereby diminishing the production rate of its very important product--fertilizer, a commodity that is already in short supply in China. A "Brief Introduction on the Content of Colloidal Silica in Natural Water in China" is attached to this report as Appendix B.

The Ion Exchange System at Qilu

During a brief examination, I found the Kurita ion exchange water treatment system (shown in Figure 1) at Qilu to be of excellent design, construction, and operation. It is state-of-the-art with respect to the production of high purity demineralized water of low conductivity and low silica content. At times, however, the system is challenged beyond its capabilities, due to the presence of colloidal silica in the groundwater. During these times some colloidal silica, it seems, passes through the entire ion exchange system and into the boilers.

Because the existing water treatment system is well designed and operated, it appears that one or more additional treatment steps will be necessary to remove the colloidal silica.

Measurement of Silica Leakage

Before implementation of any method of solution to the colloidal silica problem, soluble and colloidal silica levels should be carefully monitored at various points in the ion-exchange system. Suggested sampling points are as follows (a) cation influent, (b) cation effluent, (c) anion effluent and (d) mixed-bed effluent.

The silica monitoring should be done over a period of at least one month and possibly longer, even up to one year. To accomplish the monitoring, water samples can be taken directly and analyzed for silica. Alternatively, small hydroxide-form, macroporous anion exchange columns can be placed on the sample lines to accumulate the silica over a
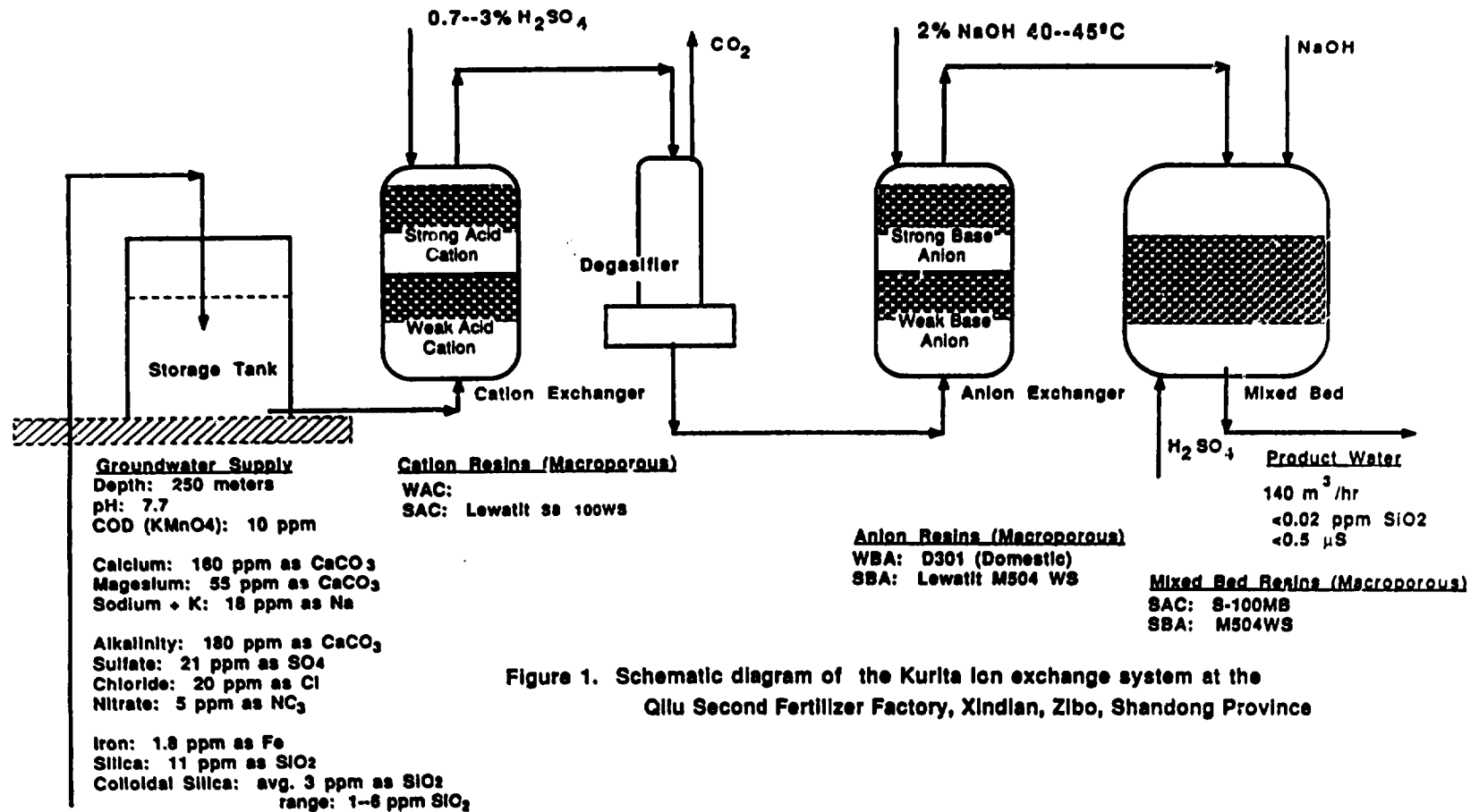
3

0.7--3% H_2SO_4

CO_2

2% NaOH 40--45°C

NaOH

Strong Acid Cation

Weak Acid Cation

Degasifier

Strong Base Anion

Weak Base Anion

Storage Tank

Cation Exchanger

Anion Exchanger

Mixed Bed

Groundwater Supply

H_2SO_4

Product Water

140 m³/hr

<0.02 ppm SiO_2
<0.5 µS

Groundwater Supply
Depth: 250 meters
pH: 7.7
COD (KMnO4): 10 ppm

Calcium: 160 ppm as $CaCO_3$
Magesium: 55 ppm as $CaCO_3$
Sodium + K: 18 ppm as Na

Alkalinity: 180 ppm as $CaCO_3$
Sulfate: 21 ppm as SO_4
Chloride: 20 ppm as Cl
Nitrate: 5 ppm as NC_3

Iron: 1.8 ppm as Fe
Silica: 11 ppm as SiO_2
Colloidal Silica: avg. 3 ppm as SiO_2
range: 1--6 ppm SiO_2

Cation Resins (Macroporous)
WAC:
SAC: Lewatit ss 100WS

Anion Resins (Macroporous)
WBA: D301 (Domestic)
SBA: Lewatit M504 WS

Mixed Bed Resins (Macroporous)
SAC: S-100MB
SBA: M504WS

Figure 1. Schematic diagram of the Kurita Ion exchange system at the
Qilu Second Fertilizer Factory, Xindian, Zibo, Shandong Province

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long period, e.g., one week to one month. This latter method cannot distinguish between colloidal and soluble silica because colloidal silica will be hydrolyzed to soluble silica during warm (45-50°C) NaOH regeneration of the small anion columns to elute the silica. It does, however, have the advantage of high sensitivity and continuous monitoring of silica. Of course, the sampling lines must be shut off during regeneration of the ion exchange system to avoid contamination by silica eluted from the resin.

Precipitation of Silica in the Weak-Base Anion Bed During Regeneration

*Special note should be taken of the following comment because I
believe it was not discussed while I was visiting the Qilu site.*

It is known that soluble silica eluted from the strong-base resin during regeneration can precipitate in the weak-base resin bed due to its acidic nature following exhaustion with mineral acids as would occur in the Qilu situation. To avoid silica precipitation in the weak- base anion bed, the first 50% of the spent caustic (NaOH) from the strong-base resin regeneration should be directed to waste. This fraction of the waste regenerant contains most of the eluted silica, and it should not contact the weak-base resin bed unless its hydroxide concentration is increased to about 2% to avoid acidification and subsequent precipitation of silica. Such precipitation of silica might be responsible for some of the silica leakage experienced at the Qilu Second Fertilizer Plant.

Clean-up of Resins in the Kurita System

A brief visual examination using the glass viewing port in the anion exchange column revealed that the anion resins had become dark brown suggesting that they are fouled with organics. An attempt should be made to clean-up the resins. This can be done using a warm (45°C) mixture of 10% NaCl and 1% HCl for regeneration followed by a double, standard regeneration with warm (45-50°C) sodium hydroxide. If this procedure does not result in removal of the organics as observed by measurement of COD in the eluent and a visual lightening of the resins, further clean-up procedures should be

attempted. The details of these further procedures can be worked out in the laboratory using small columns (25 mL) of resins exposed to various acid, base and salt solutions. In the laboratory experiments, the success of the clean-up should be determined by monitoring the COD and total silica in the eluents. The successful laboratory procedures can then be used in the full-scale column.

Colloidal Silica Removal in the United States

Colloidal silica in U.S. industrial water supplies is definitely a problem, but apparently not as big a problem as in China. Currently, colloidal silica is being removed using one or more of the following treatment processes:

1) Deep-bed, dual- or mixed-media filtration with and without coagulants.

2) Macroporous adsorbents such as anion exchange resins used as scavengers between the anion bed and the mixed bed.

3) Ultrafiltration following the mixed bed of the ion exchange system.

4) Reverse osmosis hyperfiltration preceding the ion exchange system.

Reverse osmosis requires extensive pretreatment and is only economically feasible for feedwaters of high (>500 ppm) total dissolved solids (TDS) content. RO is therefore not considered appropriate for treatment of the Qilu water.

The other three treatment methods--mixed-media filtration, macroporous scavenger resins, and ultrafiltration--should be considered as potential treatment methods to solve the Qilu colloidal silica problem.

It must be kept in mind that colloidal silica removal is not considered a solved problem in the United States. Research on all the above treatment methods is still being done. It appears that the treatment method for colloidal silica removal must be tailored to the individual water supply.

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Proposed Colloidal Silica Removal Research at Qilu

The well water at Qilu contains considerable organic matter (10 ppm as COD) and nitrate (5 ppm as nitrogen). These contaminant concentrations would be considered high for a U.S. well of this depth (250 m), and are probably due to the centuries of intensive farming of the overlying land.

In this respect, i.e., centuries of intensive farming of the land above the ground-water, the colloidal silica problem in China may be somewhat different from that in the U.S. because the silica is probably tied up in some way with the large amount of organic matter in the water. Even if the colloidal silica is not bound to the organic matter (and possibly the 1.8 ppm iron present) the organics might foul the macroporous anion resins and prevent the adsorption of colloidal silica. The same phenomena would, of course, occur in U.S. groundwaters but to a lesser extent due to lesser organics present.

The above brief discussion leads us to the conclusion that some research on colloidal silica removal is justified because of the seriousness of the problem in China and the somewhat unique aspects of their water supplies. It is recommended that silica removal research be started at Qilu using direct filtration, macroporous adsorbents and ultrafiltration. Bench-scale and pilot-scale research on these methods will allow the technical and economic comparison of these processes prior to full-scale implementation.

Direct Filtration Experiments

Direct filtration, i.e., filtration without prior coagulation and flocculation, holds the most promise for a low-cost solution to the colloidal silica problem. Dual-media (i.e., anthracite and sand) or mixed-media (i.e., anthracite, sand and garnet) filtration are recommended for treatment of the raw water after it leaves the ground storage tank and before it reaches the cation exchanger.

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Oxidation of the groundwater using air, ozone or chlorine is recommended before direct filtration. Although this is probably not essential, ferric hydroxide ($Fe(OH)_3$) would precipitate from the 1.8 ppm Fe present. The positively charged $Fe(OH)_3$ precipitate would help to remove the colloidal silica by flocculation of the negatively charged silica particles. To provide additional flocculation, alum ($Al_2(SO_4)_3 \cdot 14H_2O$) or a coagulant aid (cationic polyelectrolyte) could be used. Care must be exercised in the use of cationic polyelectrolytes because the excess polymer might pass through the filter and foul the anion exchangers.

Macroporous Adsorbent Experiments

The existing Kurita ion exchange system at Qilu contains macroporous (MR) resins throughout. These include MR weak- and strong-acid cation exchangers, and weak- and strong-base anion exchangers. These are the appropriate porosity resins for colloidal silica removal. It is possible, however, that alternative brands of resins might be better suited to the job of colloid removal. To that end it is recommended that the following U.S. resins be experimented with as replacements for, or use in addition to, the existing resins.

Rohm and Haas Resins

IRA 938	Macroporous colloidal adsorbent anion
IRA 900	Macroporous strong-base anion
IRA 93	Macroporous weak-base anion
IRA 94	Macroporous weak-base anion
IR 200	Macroporous strong-acid cation

Ionac Resins

A 642 macroporous strong-base anion

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I have contacted representatives of Rohm and Haas and Ionac and arranged to have 1-2 kg samples of these resins sent to Mr. Zhao Motang of Qilu Petrochemical Company.

Other adsorbents that could be tried for colloidal silica removal are granular activated alumina (GAAl), and granular activated carbon (GAC). To test the adsorbents and resins, small columns (300-500 cm^3) could be placed on a sampling stream following the anion exchanger and ahead of the mixed-bed. The volume of water passed through each experimental column, and the amount of silica eluted during regeneration should be recorded and compared.

Reuse of Boiler Blowdown

When colloidal silica does enter the boiler feedwater, the high temperatures causes it to hydrolyze to monomeric silica $Si(OH)_4$ which, if recycled to the ion exchange system, can be removed. This can be accomplished by flashing the boiler blowdown in a flash tank, cooling the condensate and returning it as make up water to the ion exchange system. It is good make up water because it is low in dissolved solids and contains only soluble silica that has soublized from colloidal silica. This should result in longer ion exchanger runs and less regenerant chemical usage, especially during those periods where colloidal silica is a problem and boiler blowdown is excessive.

A flow schematic of a blowdown reuse system is shown in Figure 2.
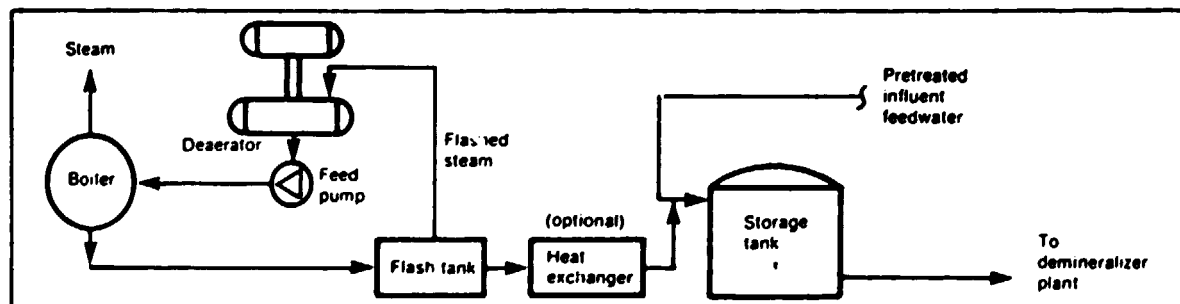
Figure 2. Re-use of Blowdown as Feed to the Demineralization System

Ultrafiltration Experiments

If a careful analysis of the silica problem reveals that silica is still leaking through the mixed-bed after cleanup of the resins and addition of a mixed-media prefilter, ultrafiltration may be the only solution to the problem. A pilot-scale ultrafilter of hollow fiber of spiral wound construction could be installed on the mixed-bed effluent and carefully monitored for silica removal performance over a period of several months. This would determine if the silica leakage was truly colloidal silica and whether a full-scale ultrafilter would eliminate the leakage.

If justified by pilot-scale experiments a full-scale ultrafilter could be installed as a means of last resort to eliminate the colloidal silica problem. The reject water from the cross flow ultrafiltration system could be recycled to the ion exchange system after passing through the mixed-media prefilter.

APPENDIX A

BRIEF INTRODUCTION
ON CONTENT OF COLLOIDAL SILICA IN NATURAL WATER
IN CHINA

Prepared by
The Staff of the Second Fertilizer Factory of
The Qilu Petrochemical Company

Many factories in China have found that colloidal silica is exists in the n. ˙ural water used in their factories. A preliminary survey made only from power industry and petrochemical industry is shown in the following table:

TABLE 1. COLLOIDAL SILICA IN CHINA

Factory Name	Water Source	Content of Colloidal Silica ppm	Location
Laiwu Thermal Power Plant	Well	3-4	Shandong
Pingdingshan Thermal Power Plant	Reservoir	2.1	Henan
Yuanbaoshan Thermal Power Plant	Well	0.5-3.6	Inner Mongolia
Minhang Thermal Power Plant	River	1.0	Shanghai
No. 2 Fertilizer Factory Qilu Petrochemical Corp.	Well	1-3	Shandong
Qianjin Chemical Factory Yanshan Petrochemical Corp.	Well Reservoir	14	Beijing

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These factories have gradually acknowledged the importance of the removal of colloidal silica from natural water to avoid the threat to their safety and full-load production. For example, the No. 2 fertilizer factory, Qilu-Petrochemical Corp., is one of the large-sized leading enterprises in China. The increased content of colloidal silica in the well water in April, 1982, resulted in a SiO_2 content in steam beyond the criterion, and the factory was forced to reduce operating load. Qianjin Chemical Factory, Yanshan Petrochemical Corp., is also among the larger-sized leading enterprises owned by the State. Due to the increased content of colloidal silica in their natural water in April, 1985, the content of SiO_2 in steam exceeded the criterion, and the factory was forced to shut down for overhaul, too. Both of the above mentioned factories sustained great economic losses due to colloidal silica. Many of China's power plants are faced with the same problems. Therefore, treatment of colloidal silica in natural water is a very important problem that urgently needs to be solved.

APPENDIX B

35 mm SLIDES PRESENTED TO THE
TECHNICAL STAFF OF THE
SECOND FERTILIZER FACTORY
QILU PETROCHEMICAL COMPANY
XINDIAN, ZIBO CHINA

DURING
THE LECTURES
ON

THE REMOVAL OF COLLOIDAL SILICA

BY
PROFESSOR DENNIS CLIFFORD
DIRECTOR OF ENVIRONMENTAL ENGINEERING
UNIVERSITY OF HOUSTON
HOUSTON, TEXAS 77204   U.S.A.

JULY 3--5, 1988

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THE REMOVAL
OF
COLLOIDAL SILICA FROM WATER

by
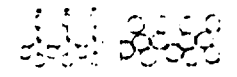
Dr. Dennis Clifford
University of Houston
Houston, Texas   U.S.A.

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胶状硅脱除技术

丹尼斯·克利福德博士

美国. 休斯顿大学

The Definition of "Silica"
Reported as silicon dioxide (SiO_2)

includes crystalline (quartz)

amorphous, hydrated ($SiO_2 \cdot H_2O$), and hydroxylated ($\equiv SiOH$) forms

silicic acid: $Si(OH)_4$

Total Silica = Soluble Silica   + Insoluble Silica
                   $Si(OH)_4$ quartz + colloidal

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Soluble and Colloidal Silica

Soluble silica	=	$Si(OH)_4$, monosilicic acid
Polysilicic acid (also "soluble")	=	Polymerized SiO_2 up to 100,000 MW (oligomers)
		< 50 Å diameter (<0.005 µm)
Colloidal silica	=	Highly polymerized SiO_2
		> 50 Å diameter (>0.005 µm)

Colloidal (Amorphous) Silica

Particle diameters > 0.005 μm

Most colloidal silica will pass a 0.45 μm filter
   Not possible to determine colloidal silica by
   membrane filtration technique (0.45 μm filter)

Non-molybdate reactive silica

Isoelectric point (IEP) at pH ~ 2
   Negatively charged (anionic) above pH 2
   Positively charged (cationic) below pH 2

Presumably cationic species can exist at low pH
   $\equiv SiOH + H^+ = \equiv SiOH_2^+$

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The Dissolution of Quartz or Colloidal Silica

$$SiO_2 + 2 H_2O = Si(OH)_4$$

$Si(OH)_4$ = soluble monomeric silica

$$\begin{array}{c} OH \\ | \\ HO\text{-}Si\text{-}OH \\ | \\ OH \end{array}$$
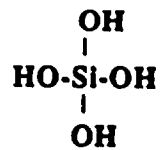
Solubility of amorphous silica at pH 7 = 120 ppm
   Solubility of quartz at pH 7 = 6 ppm

元定形玻 的溶解机理
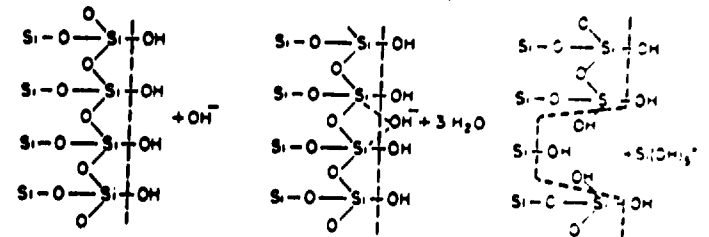
Mechanism of dissolution of amorphous colloidal silica

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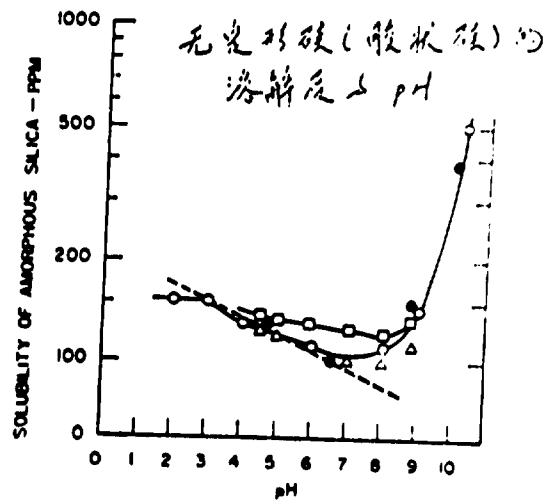
The solubility of amorphous silica vs pH at 25°C

Soluble Silica

$$Si(OH)_4 = Si(OH)_3O^- + H^+$$
silicic acid   silicate   proton

$$\frac{[H^+]\,[Si(OH)_3O^-]}{[Si(OH)_4]} = K_a = 10^{-9.8}$$

$-log\ K_a = pK_a = 9.8$ @ 25°C

$pK_a = 9.2$ @ 90°C

Properties of Soluble Silica, Si(OH)$_4$

Reacts rapidly with molybdic acid to form yellow silicomolybdic acid

Non-ionic, weakly acidic (pK$_a$ = 9.8)

Not transported by electrical current

Si(OH)$_4$ is volatile at high temperature (carryover) leading to turbine blade deposits

Si(OH)$_3$O$^-$ anion is non volatile

Methods of Silica Analysis

Total Silica = Colloidal Silica + Soluble Silica

Total Silica: Gravimetric method (SiF$_4$ volatil.)
               Atomic Absorption (GFAA; 250.7 nm)

Soluble Silica: molybdate reactive (yellow)
                  reduced complex (blue)

Colloidal Silica: non reactive determined by
                      difference (total - soluble)

Analysis for Soluble Silica, Si(OH)$_4$ and Oligomers

Soluble silica + Molybdic acid + water
       = β-Silicomolybdic acid (yellow)

$$7\ Si(OH)_4 + 12\ H_6Mo_7O_{24}\cdot4H_2O + 126H_2O$$
$$= 7\ H_8Si(Mo_2O_7)_6\cdot28H_2O$$
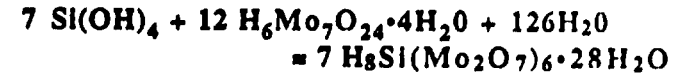
Reduced molybdenum blue method: 10x sensitivity
Polysilicic acid and colloidal silica do not react

Processes for Removal of Soluble Silica from Water

Strong-base anion exchange resin

Co-precipitation/adsorption with metal hydroxides
Fe^{3+}, Al^{3+}, Mg^{2+}, Mn^{4+}
Co-precipitation with $Mg(OH)_2$ is best

Reverse Osmosis (RO)

Ineffective Processes are
Microfiltration, Ultrafiltration
Cation exchange
Weak-base anion exchange
Electrodialysis
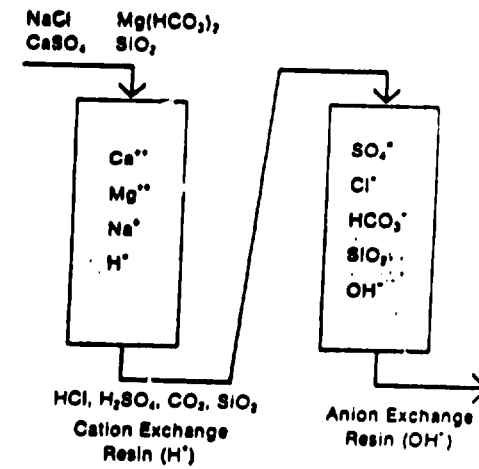
Strong Base Anion Exchange for Silica Removal

$$\overline{R^+OH^-} + Si(OH)_4 = \overline{R^+Si(OH)_3^-} + HOH$$

where: R^+ = ----$N(CH_3)_3^+$ (Type 1 SBA) or
-----$N(CH_3)_2CH_2OH$ (Type 2 SBA)

Resin can be gel or macroporous (MR)
gel resins remove soluble silica and oligomers
MR resins remove soluble and colloidal silica

Silica elutes from the column before all other ions
Selectivity sequence for the common ions is
$$SO_4^{2-} > NO_3^- > Cl^- > HCO_3^- > Si(OH)_3^-$$

Two-Bed Delonization Train.
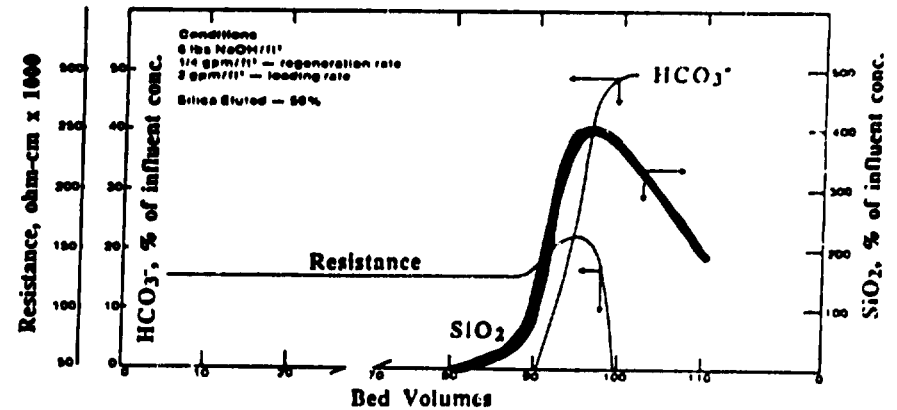
Breakthrough curves for HCO_3^- and SiO_2 from A-641 SBA Resin
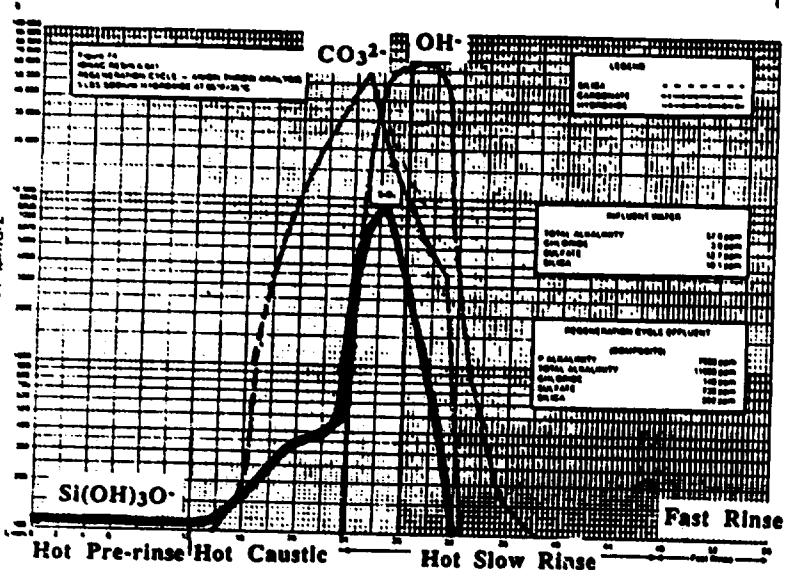
Elution of silica, carbonate and hydroxide during anion regeneration

Effect of temperature on solubility of SiO_2 (pH 7)

无定形硅的溶解速率

The rate of dissolution of amorphous silica vs pH
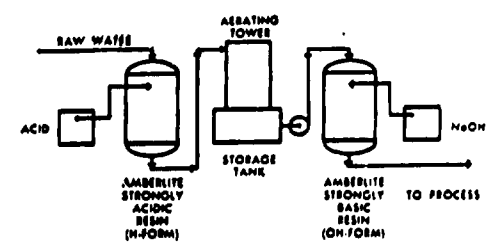
Two-Bed Strong-acid, Strong-Base Deionization System

Regeneration of a Mixed-Bed

| SERVICE | BACKWASH | SIMULTANEOUS REGENERATION | MIXING |

typical arrangement of a deionization
unit using Monobed resins
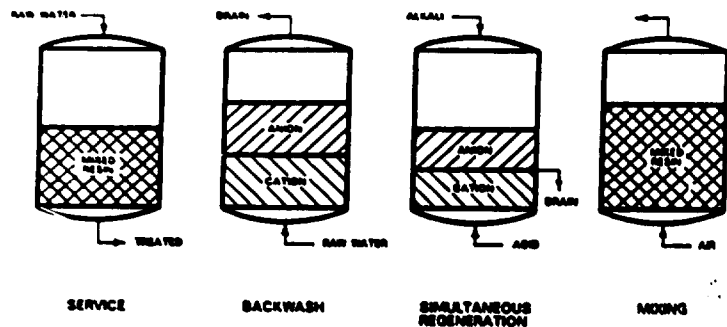
Typical Performance of Deionizer Systems
Based on waters with less than 500 ppm TDS

	SYSTEM			
	Two-Bed	Four-Bed	Mixed-Bed	Two-Bed Plus Mixed Bed
TDS. ppm	2.0-3.0	0.2-1.0	0 2-0 5	04-0 10
Silica (as SiO₂), ppm	.01-.10	.01-.05	.01-.05	01-05
Conductivity, micromhos	2	1	.25-1.0	.07-25
Specific Resistance, ohms—cm	500,000	1,000,000	1,000,000-4,000,000	4,000,000-15,000,000
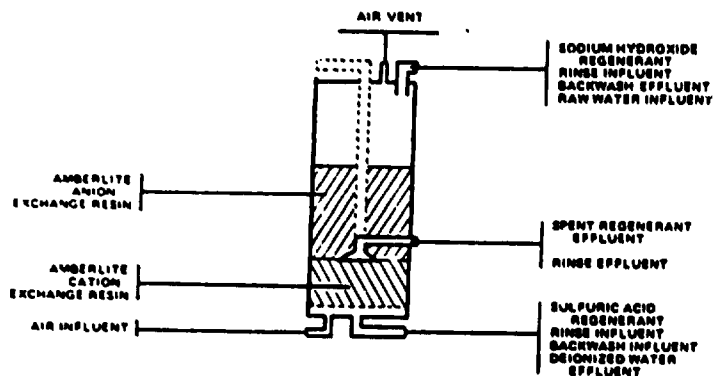
Hot Lime Softening for Silica Removal

$$Ca(OH)_2 + Ca(HCO_3)_2 = 2\ CaCO_3 + 2\ H_2O$$

$$2\ Ca(OH)_2 + Mg(HCO_3)_2 = Mg(OH)_2 + 2\ CaCO_3 + 2H_2O$$
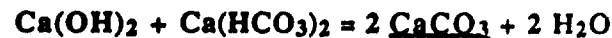
Silica removal depends on magnesium concentration
Sludge recirculation is essential
Freshly precipitated $Mg(OH)_2$ is required
Temperature approximately 100°C necessary
Large amounts of MgO are usually added
Optimum pH in the range of 10-11 (quite high)

Both colloidal and soluble silica are removed

Silica reduction by hot process (100°C) lime softening
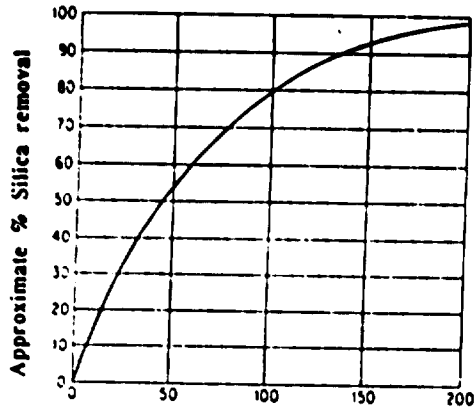
(x-axis: Magnesium precipitated, ppm as CaCO₃; y-axis: Approximate % Silica removal)
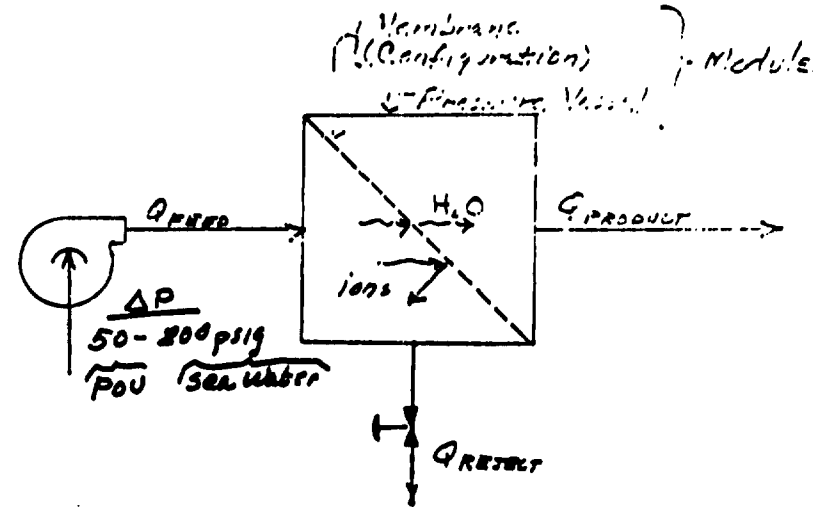
Reverse Osmosis (RO) for Silica Removal

Excellent removals expected for CA & TFC
>95 % of soluble silica
100 % removal of colloidal silica

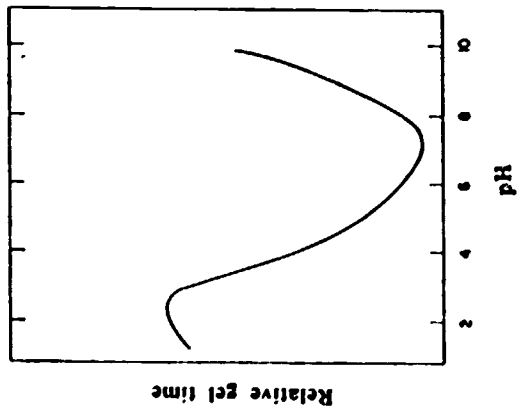Avoid SiO_2 > 120 ppm in brine, optimum pH for RO (6.0) is also the optimum pH for SiO_2 ppt

Costs are high, pretreatment requirements severe, and reject water is 20-50% of feedwater

RO SCHEMATIC

Water Flow

$$Q_W = Q_P = \frac{K_w A}{S}(\Delta P - \Delta \pi) = W_P (\Delta P - \Delta \pi)$$

Salt Flow

$$\dot{M}_s = Q_s = \frac{K_s A}{S}\Delta C = S_P \Delta C$$

Yield

$$Y = \frac{Q_P}{Q_F}100 \qquad SP = \frac{Salt\ passage}{} = \frac{C_E}{C_F}10$$

$$SR = \%\ Salt\ Rejection = \left(\frac{C_F - C_P}{C_F}\right)100 = 100 - SP$$

Hydroxide catalyzed bond formation
between colloidal silica particles

Effect of pH on the
polymerization of silica

Ultrafiltration (UF) for Silica Removal

UF removes colloidal but not soluble silica

UF also removes high MW organics, aquatic humus

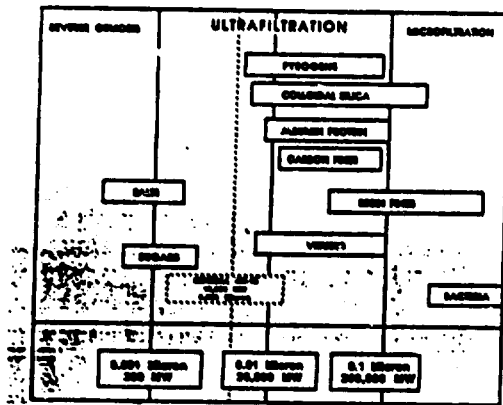Fouling by silica gel is possible

Reject stream is 10% or more
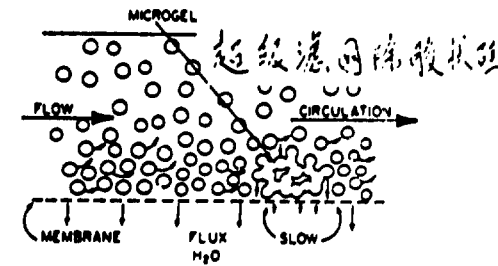
Too expensive for large scale

Extensive pretreatment may be required
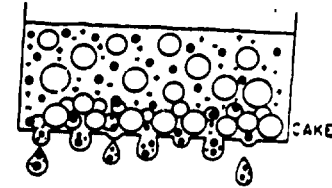
Typical microfiltration with 0.10--10 μm pores

THE ULTRAFILTRATION SPECTRUM

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Ultrafiltration to remove colloidal silica

Processes for Removing Colloidal Silica

Flocculation with metal hydroxides
Fe^{3+}, Al^{3+}, Mg^{2+}

Flocculation with polymers
Cationic polyelectrolytes (quat. polyacryl.)
Non-ionic polymers (polyethylene oxide)

Macroporous strong-base anion resins (IRA 938)

Gel and macroporous strong acid cation resins
Apparent removal of the positively charged
colloid at pH < 2, the IEP

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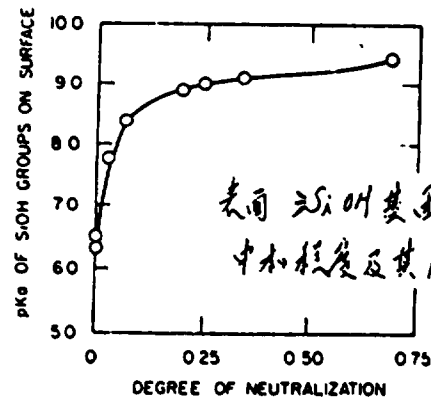
pKₐ of surface silanol, $\equiv SiOH$, groups on colloidal silica

(graph axis labels: pKₐ OF SiOH GROUPS ON SURFACE; 100, 90, 80, 70, 60, 50; DEGREE OF NEUTRALIZATION; 0, 0.25, 0.50, 0.75)

表面 $\equiv Si$ 州 类剂的
中和程度及其 pKₐ值

Coagulation and Flocculation for Silica Removal

$Al(OH)_3$ removes soluble and colloidal silica
$Al/SiO_2 = 4/1$, pH = 8-9 for soluble silica
Soluble silica removed by precipitation
$Al/SiO_2 = 1/40$; pH = 4-5 for colloidal silica
Colloidal silica removed by flocculation

$Fe(OH)_3$ reportetdly "good" for silica removal
Should behave similarly to $Al(OH)_3$
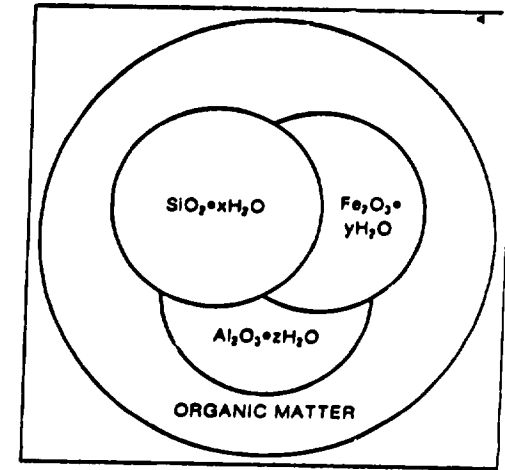Possibly higher pH optimum for $Fe(OH)_3$

High molecular weight cationic polyelectrolytes
Bridging flocculation in pH range 3-9

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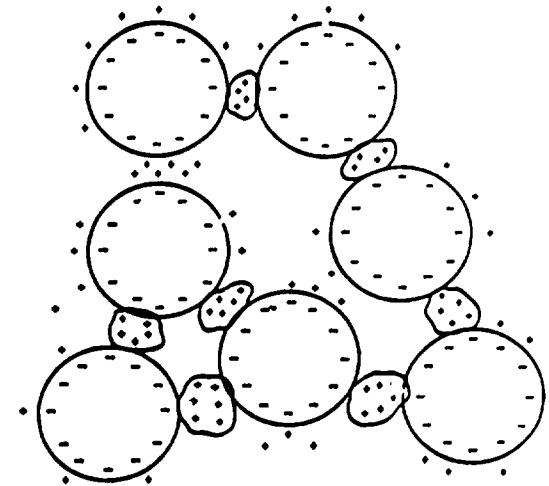
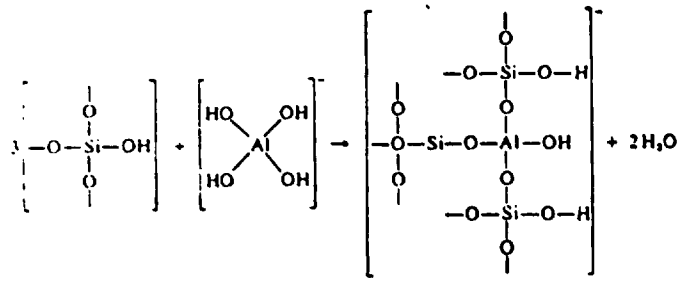Flocculation of silica particles by colloidal particles of opposite
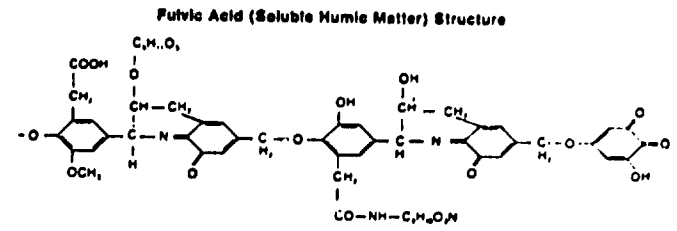charge, e. g., $\equiv Al(OH)_2^+$ or $\equiv Fe(OH)_2^+$
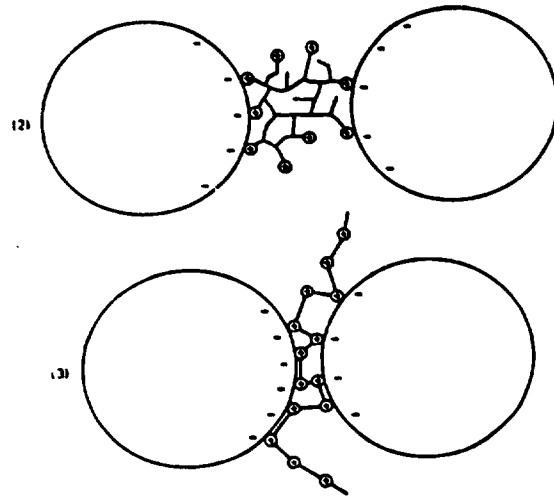
Flocculation of colloidal silica particles by:
(2) cationic 3-dimensional polyelectrolyte
(3) cationic linear polyelectrolyte

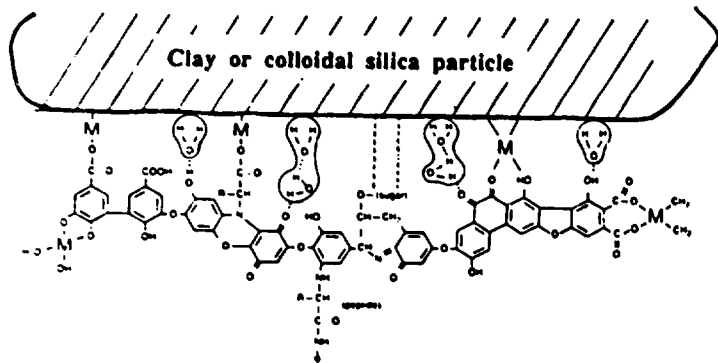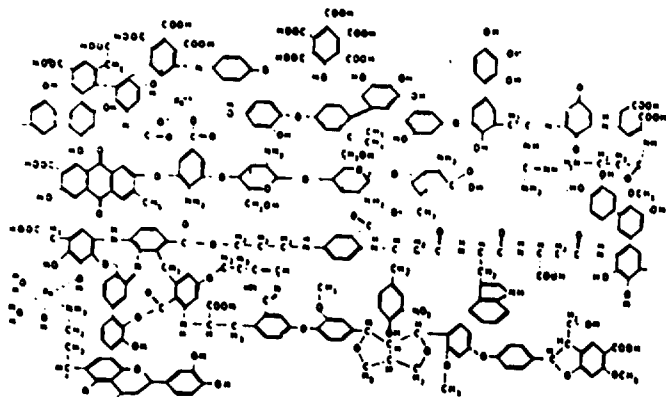The reaction of colloidal silica with
aluminum hydroxide

The Universal Colloid

Fulvic Acid (Soluble Humic Matter) Structure

Humic Acid (Insoluble) Humic Matter Structure

CLAY-HUMATE OR SILICA-HUMATE COMPLEX

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Water Quality at Secondary Fertilizer Factory, Qilu

Cation	ppm as $CaCO_3$	Anion	ppm as $CaCO_3$
Ca^{2+}	160	HCO_3^-	180
Mg^{2+}	55	Cl^-	28
Na^+/K^+	39	SO_4^{2-}	22
		NO_3^-	4

Fe^{2+}	1.8 ppm as Fe
SiO_2	11.0 ppm as SiO_2
Colloidal SiO_2	3.0 ppm as SiO_2
COD ($KMnO_4$)	10.0 ppm
pH	7.7

Current Status of Indust ial Water Treatment

Water consumption
   Plant # 1 = 160 m^3/hr; Plant #2 = 140 m^3/hr

Water quality requirememts
   SiO2 ≤ 0.02 ppm;   Conductivity ≤ 0.5 μS

Ion Exchange System
   SAC Type I S8-100ws
   SBA M 504 ws
   WBA D301 (Domestic Product)

Ways to Improve Silica Removal

Better pretreatment of the raw water:
- Oxidation (Air, O_2, or Cl_2)
- Coagulation (Fe^{3+}, Al^{3+}, or cationic polymer)
- Flocculation (Gentle mixing for 20 min)
- Sedimentation (Quiet settling for 90 min)
- Filtration (Possibly, direct filtration can replace the flocculation and sedimentation steps; use dual or mixed media)
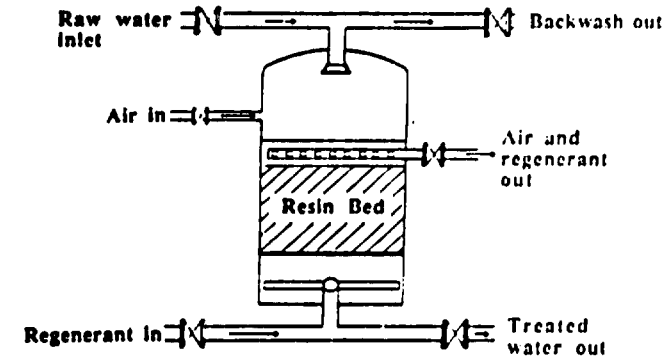
Countercurrent regeneration of anion exchanger
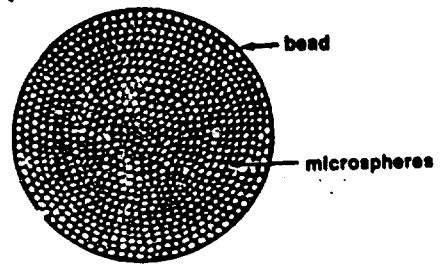**MR cation exchangers to adsorb + colloids**
MR anion exchangers to adsorb - colloids
Super MR (IRA 938) Scavenger SBA resin

COUNTERCURRENT FLOW REGENERATION
(The usual regeneration is co-current but it leads to higher leakage)

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MACROPOROUS RESIN STRUCTURE