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UNIVERSITY OF ALBERTA

SILICA REMOVAL FROM HEAVY OIL PRODUCED WATER BY THE HYDROGARNET PROCESS

BY

EBENEZER ANTWI

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE
IN
MINERAL ENGINEERING

DEPARTMENT OF MINING METALLURGICAL AND PETROLEUM
ENGINEERING

EDMONTON, ALBERTA
SPRING 1993

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Date 10TH FEB 1993

DEDICATION

Dedicated to

Jane and Ruth, Paapa Kwaku Kwao and Maame Abena Aniniwa, Felicia and Salome, Kwaku Antwi, G.M. Ansong and E.S. Boadi for thier great help and inspiration.

ABSTRACT

In Alberta, Canada, the production of heavy oil is mainly achieved by steam- based in-situ enhanced oil recovery operation which results in the coproduction of large quantities of contaminated water generally referred to as "Produced Water". This produced water is usually injected into deepwell formations for disposal. Such an operation may be economically and environmentally satisfactory in an area of plentiful water supply and unlimited capacity for deepwell disposal but the luxury of these resources do not exist in Alberta. Thus the only alternative is to treat and recycle the produced water for continuous oil production. Produced Water contains large amounts of impurities and of these impurities, dissolved silica and silicates are the most difficult to remove during wastewater treatment. Hot lime softening is currently being advocated as the an effective method for silica removal from briny produced water. However, due to high capital cost and serious environmental problems resulting from the generation of alkaline sludge in this process, much more research attention have been given to alternative processes for produced water treatment.

In this study, silica removal from produced water using tricalcium hydroaluminate precursor (hydrogarnet process) was investigated. This hydrogarnet process utilizes the conversion of dissolved silica into filterable calcium aluminosilicate precipitate. Kinetics studies reveal that the reaction is first order and proceeds via initial adsorption of silicates onto the surface of the precursor matrix to form hydrated calcium aluminosilicates known as hydrogarnet. The presence of carbonate and bicarbonate ions was found to be deleterious to the desiliconization reaction due to the dissolution of the hydroaluminate precursor. Finally, the use of weakly acidic hydrogen form ion exchange resin was found to be a very effective polishing step after desiliconization reaction.

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TABLE OF CONTENTS

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

FIGURE PAGE

LIST OF PLATES

PLATE PAGE

1.0 INTRODUCTION

The Province of Alberta is endowed with rich oil resources,however while some of the oil resources occur as conventional deposits, a major proportion is in the form of heavy oil and oil sands deposits. Most of the conventional light crude deposits are being depleted rapidly, hence more attention has been focused on the exploitation of the non-conventional oil deposits. These non-conventional oil deposits which are thick, viscous, and relatively high in sulphur content are referred to as bitumen or heavy oil. Heavy oil deposits are mainly exploited by enhanced oil recovery methods. Enhanced oil recovery refers to the production of crude oil from reservoirs through the application of pressure by waterflooding, gas injection, polymer flooding, caustic injection, steam flooding, cyclic steam injection and related methods[1]. Conservative estimates indicate that current heavy oil production of 100, 000 barrels per day (bpd) are expected to rise to above 500,000 bpd within the next decade[1,2,3,4].

Produced water as the name implies, is the wastewater co-produced with oil from in situ enhanced oil recovery processes such as steam flooding, cyclic steam stimulation and water flooding[2]. Currently, the term is used in a broader sense to encompass all oily wastewater from oil platforms[1,2]. Produced water usually contains two major classes of impurities, namely, total dissolved solids (TDS) and dissolved silica or silicates. Total dissolved solids include mainly salts of sodium, potassium, calcium, and magnesium. These impurities are due to the dissolution of inorganic rock minerals in the injected steam. The presence of these impurities preclude the recycling of the produced water through steam generators, or their direct discharge into the environment.

In Alberta, heavy oil production is mainly achieved by thermal recovery methods that include both steam based in-situ enhanced oil recovery processes as well as in-situ combustion. While in-situ combustion may require little or no water, the steam-based methods require large quantities of fresh water[3,4].

The fresh water requirements in heavy oil production are mainly for steam generation and production inlet cooling. During in-situ production, the required steam-to-oil ratio (SOR) can vary from 2:1 to 20:1, depending on the reservoir characteristics. However, an average SOR of 5:1 is generally obtained in Alberta[3,4]. This means that at a heavy oil production rate of 500,000 bpd, at least 2 million barrels or 320, 000 m^3 of water is needed per day. In addition to placing heavy demands on fresh water resources, this level of water usage will create massive wastewater problems, as most of the injected steam is coproduced with oil and impurities[1,14].

The treatment of industrial wastewater is currently a subject of intense research around the world, and several studies are being conducted to investigate the removal of dissolved silica and TDS from produced water, municipal water, raw water for industrial and domestic use, and aluminate solutions in the production of alumina. For example, Scharwtz[5] developed a method for silica removal from municipal and industrial water using the adsorption of silica by the addition of ferric sulphate with lime and soda ash. Calise et al [6] have studied the warm and hot processes, using the adsorption of silica on activated magnesia (MgO) and Zeolite for silica removal. Applebaum[7] have reported a salt-splitting technique which utilizes a strong basic anion exchanger for the removal of silica from industrial water. Theoretically, a strongly basic anion exchange resin could be used to remove silica but no resin exists that could be used to remove silica selectively, and in waters which contain large quantities of chloride, (eg produced water)the cost will be prohibitive.

Attempts have also been made to remove silica and TDS from seawater and brackish water by using membrane processes such as ultrafiltration and reverse osmosis. Furthermore, other investigators such as Norworyta[8] have studied another method for silica removal from aqueous aluminate solutions, using the adsorption of silica by tricalcium hydroaluminate to form a stable precipitate called hydrogarnet, which exerts a catalytic effect on further desiliconization reaction.

Other studies have investigated the use of vapour compression evaporation in the removal of TDS but this method does not give satisfactory results. The produced water generated in most Canadian enhanced oil recovery facilities is presently not treated and cannot be recycled to once - through steam generators. However, Esso Petroleum Canada has applied the hot lime softening(HLS) process to treat produced water for recycling to steam generators[9].

The industrial application of the HLS process has revealed a number of serious problems such as high capital cost and the production of large quantities of highly toxic alkaline sludge which makes it environmentally hazardous to use conventional solid waste disposal methods such as land fill. The seriousness of the problems associated with the HLS process has resulted in the search for alternative treatment methods. A promising alternative technology involve silica removal by the hydrogarnet process. This technique has been successfully used for the removal of dissolved silica from hydroaluminate solutions, but has not been applied to the removal of silica from produced water. Research studies in the application of the hydrogarnet process for silica removal from produced water was recently developed by Dr. Nosa O. Egiebor. This novel hydrogarnet technique of silica removal from produced water forms the main study in this work.

Produced water samples from three enhanced heavy oil operations (Esso Cold Lake, Amoco Lindberg, Shell Peace River) were obtained and used for this study.

The primary objectives of this study were:

1. To investigate the effectiveness of the hydrogarnet process using a tricalcium hydroaluminate precursor for silica removal from typical produced water samples from Alberta.
2. To study the effect of temperature on the kinetics and mechanism of the silica removal.
3. To study the effect of varying amounts of the tricalcium hydroaluminate precursor on the rates of desiliconization
4. To determine the effect of other chemical properties of the produced water such as carbonate and bicarbonate contents as well as hardness on the desiliconization reaction.
5. To study the physical characteristics of the desiliconization reaction precipitate

2.0 LITERATURE SURVEY

2.1 DESCRIPTION OF HEAVY OIL AND BITUMEN(TAR SANDS) RESERVES AND PRODUCTION IN ALBERTA

The worldwide conservative estimate of oil in place is vast and is said to be about 653 billion cubic metres[1,2,4]. In Alberta, there is about 270 billion cubic metres of bitumen in place in the oil sands and carbonate formations and about one billion cubic metres of heavy oil[4,14]]. Thus Alberta holds over 40% of the reported bitumen and heavy oil reserves in the world. In contrast to the bitumen and heavy oil reserves, Canada has only 1.1% of the world's light and medium crude oils[4].

Alberta's massive crude bitumen and heavy oil resources or deposits lie predominantly in the eastern half of the province forming a belt stretching from the oil sands in the Athabasca formation to the heavy oils in the south. The deposits are contained in Lower Cretaceous unconsolidated sands and the Upper Devonian carbonate sedimentary formations in the Athabasca, Cold Lake and Peace River oil sands areas. The Grosmont Carbonate formations also contain large amounts of bitumen[4,11,14]. Figure 1 shows the general map of Alberta and the locations of the major oil sands and heavy oil deposits[4].

Table 1 also shows the summary of the geological attributes of the oil sand deposits[14]. Of these reserves, less than five percent are deemed to be exploitable by open pit mining. This surface mineable area, defined by economic stripping ratio criteria lies only in the northern section or part of the Athabasca oil sands area. Thus, the vast majority of Alberta's oil sands and heavy oil deposits may only be exploitable through in -situ recovery technology.

TABLE 1

SUMMARY OF GENERALIZED GEOLOGICAL ATTRIBUTES OF OIL SANDS AND HEAVY OIL IN ALBERTA

			Depth range (m)	Average pay thickness (m)	API °	Average porosity (%)	Depositional environment	Dominant grain minerals
ATHABASCA	Grand Rapids	Upper	200 - 400	9	8	30	Shoreline and Shallow Marine	Quartz Chert Feldspar Rock fragments
		Middle	230 - 430	5	8	30		
		Lower	270 - 470	6	8	30		
	Wabiskaw/ McMurray	Mineable	0 - 120	38	8 - 10	29	Continental to Marine Shelf	Quartz
		In Situ	80 - 750	19	8 - 10	28		
COLD LAKE	Grand Rapids	Upper	275 - 500	6	11 - 15	30	Continental to Marine Shoreline	Quartz Rock fragments Feldspar
		Lower	325 - 525	12	9 - 12	31		
	Clearwater		375 - 500	12	10 - 11	30	Marine Shoreline	Quartz Feldspar Rock fragments Altered grains
	Wabiskaw / McMurray		425 - 600	5	10 - 12	25	Marine Shelf / Continental	Quartz Glauconite / Quartz
PEACE RIVER	Bluesky / Gething		460 - 760	14	9	24	Estuarine to Shallow Marine	Quartz Chert Rock fragments
CARBONATE DEPOSITS	Debolt		500 - 800	32	8 - 10	18	Open Marine	Limestone Dolomite
	Shunda		500 - 800	14	8 - 10	20	Tidal Flat to Open Marine	Limestone Dolomite
	Grosmont		260 - 350	16	7	16	Tidal Flat to Open Marine	Dolomite

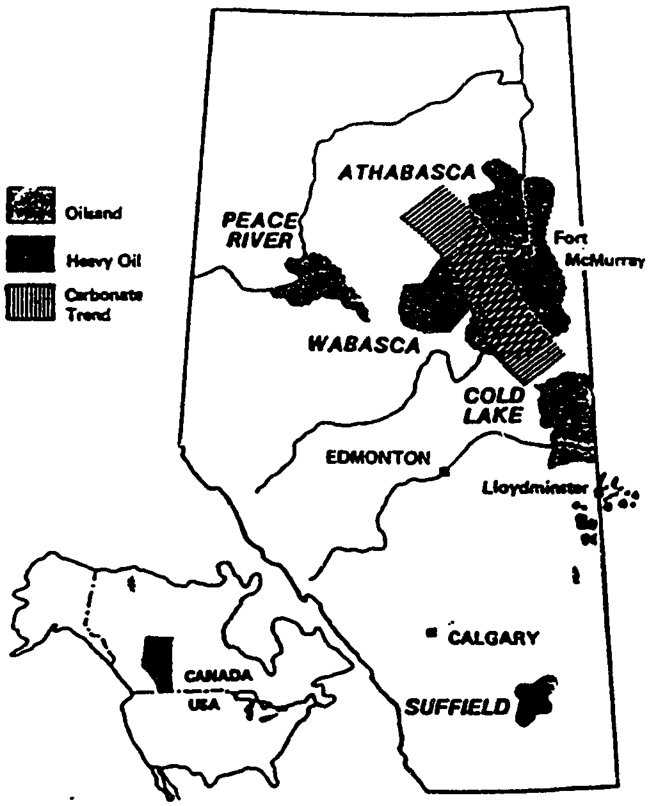


Figure.1. Site and Location of Heavy Oil and Bitumen Production Areas in Alberta

The origin of Alberta oil sands hydrocarbons has been the subject of much discussions and debate over the years, but it is now generally accepted that the bitumen was originally emplaced as a lighter hydrocarbon which has subsequently undergone significant in-situ degradation following migration from some distant area[14]. Furthermore, the oil sands deposits of Alberta differ substantially in terms of the environmental conditions under which they are deposited[14]. This variability is in turn reflected by differences in reservoir geometry, lateral and vertical continuity, internal fabric, and mineralogical composition. These elements influence the relative distribution and saturation of reservoir fluids, and most importantly, the degree to which the reservoir responds successfully to various thermal stimulation processes[14,15].

Light oil production in Alberta appears to have peaked and bitumen production has been increasing with bitumen and synthetic oil now making up about 20 percent of Canada's total production of crude oil. About 43,000 cubic metres of oil is produced daily and 15,000 cubic metres per day of that oil is produced by enhanced oil recovery methods such as thermal in situ recovery methods[4,11,14]. The remainder of the 43,000 cubic metres per day are produced from the surface oil sands at the Syncrude and Suncor operation near Fort McMurray. The bulk of thermal in situ production of bitumen comes from three commercial projects. The largest is the Esso Resources development at Cold Lake which produces about 13,000 cubic metres per day. BP Canada and Petro-Canada jointly produce 1000 cubic metres per day of bitumen at Wolf Lake in the Cold Lake oil sands. Shell Canada PREP project, in the Peace River oil sands, produces about 1600 cubic metres per day of bitumen[4,14,18]. Graphs of viscosity verses temperature for oil including the initial reservoir temperature[4] from each of the oil sands and several typical heavy oil deposits are shown in Figure.2.

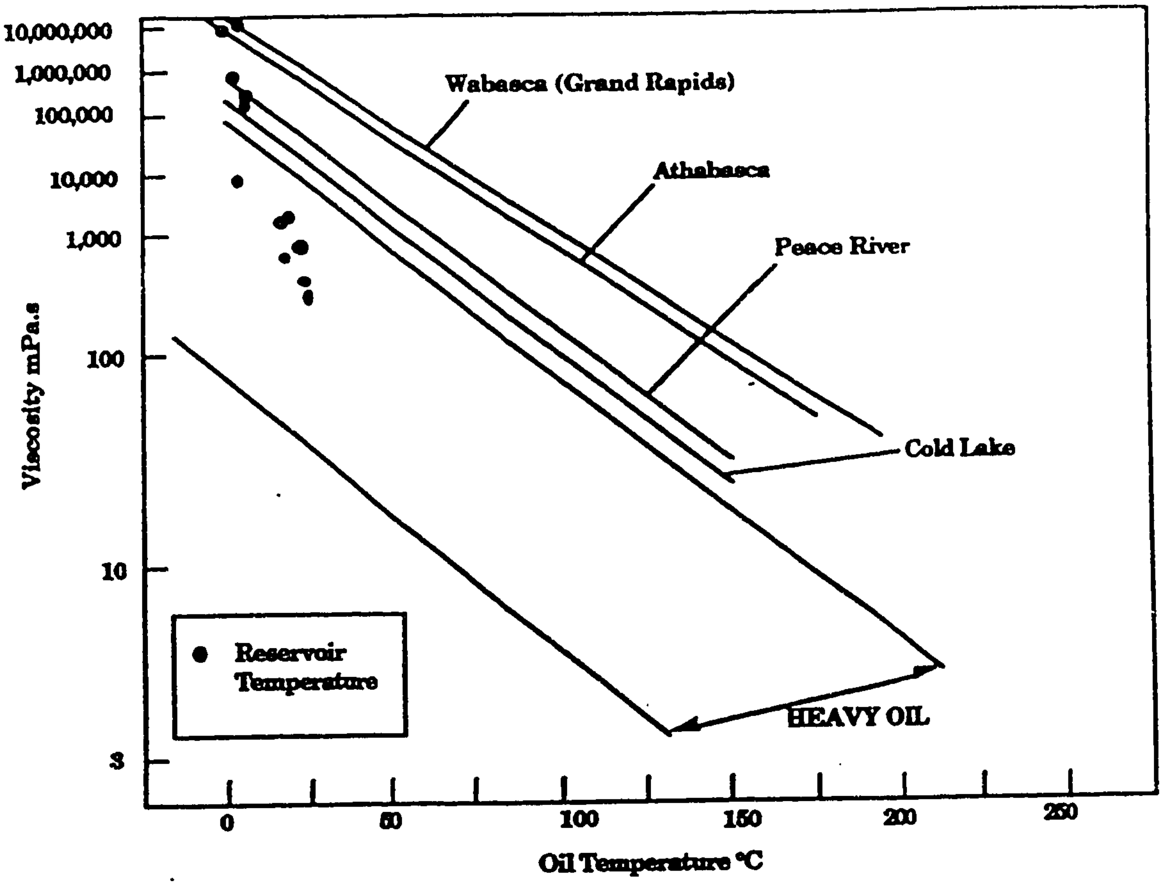


Figure 2. Viscosity and Temperature Relationship of Bitumen and Heavy Oil

Although the oil viscosities are very high at initial reservoir conditions, the curves illustrate the significant reduction of viscosity with increasing temperature. This is the reason why enhanced oil recovery methods such as thermal in situ recovery processes are fundamental in recovering this oil particularly in the oil sands deposits. Experience has shown that a number of different recovery processes may be necessary to recover the majority of bitumen and heavy oil, and that combinations and innovative modifications are often necessary to find a process which will work in specific locations[1,2,14,15,18].

2.2 ENHANCED OIL RECOVERY METHODS

When first brought into production , most conventional and heavy oil reservoirs have sufficient natural forces to mobilize the oil out of the oil bearing rocks to the production wells. During this primary production phase, the advance of underground water beneath the oil, forces the oil towards the well. Alternatively, natural gas dissolved in the crude may expand to force the oil out of the rocks. However, these natural forces are soon depleted, and the oil production drops sharply. In order to improve production, it is common practice to use enhanced oil recovery methods[14,15].

This oil recovery technique is designed to increase the production rate and the ultimate recovery of viscous crude oils. Enhanced Oil Recovery methods can be subdivided into three major categories and is presented schematically in Figure 3. In practice, most of the different enhanced oil recovery methods are used in combination with one another. However for the purpose of this work, only the thermal recovery processes will be further described in detail..

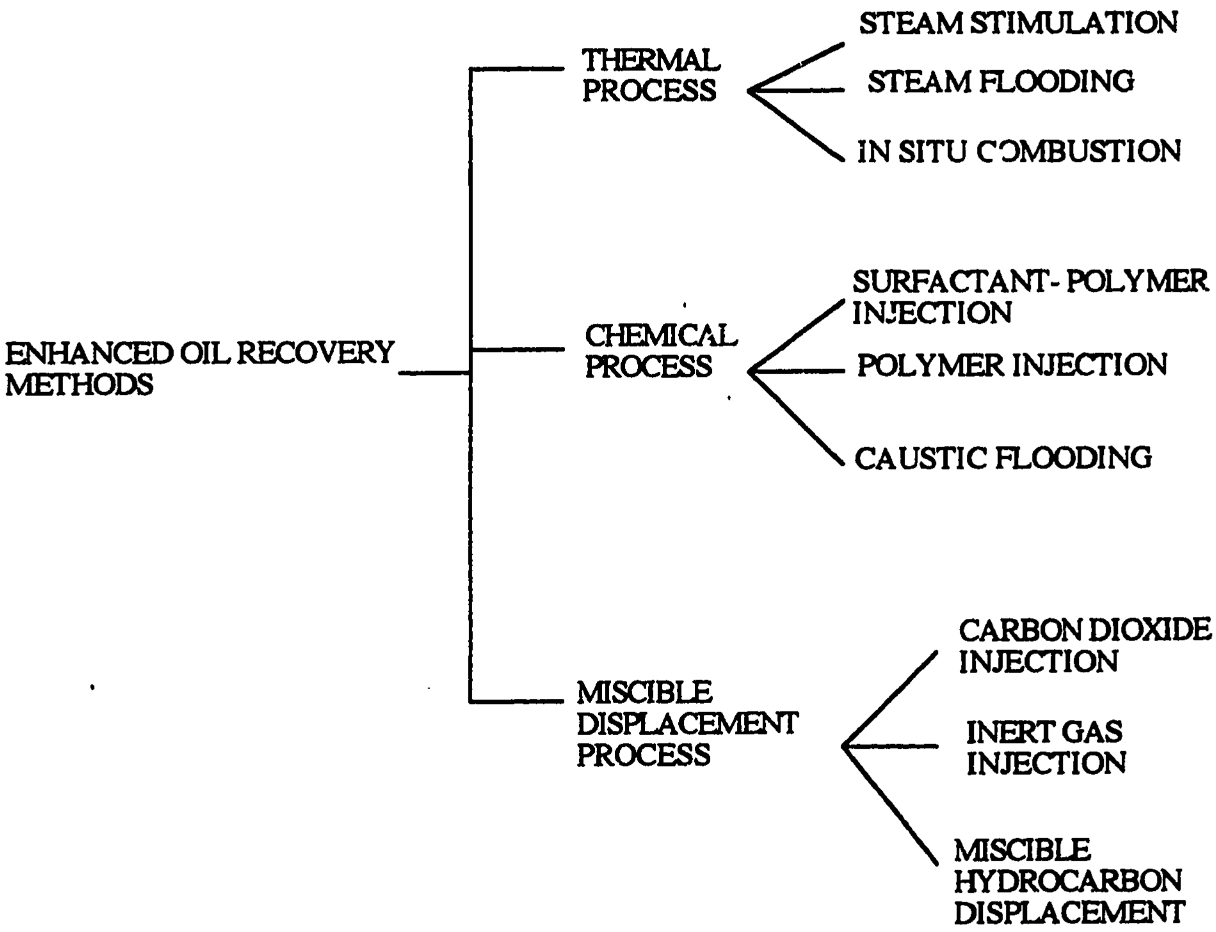


Figure 3. Flowsheet of Enhanced Oil Recovery Methods

2.2.1 THERMAL RECOVERY METHODS

The primary function of thermal recovery methods is to reduce the viscosity of the in-place oil. In the process, many reservoir volumes of hot water, steam or air are injected in the reservoir which further enhances the driving forces[15]. The capillary forces are not directly affected by the heat, but when the oil trapped by the capillarity is heated, its light fractions are distilled and become mobile. Steam injection is currently the principal enhanced oil recovery method[14,15].

The main advantage of steam injection over other enhanced oil recovery methods is that, steam can be applied to a wide variety of reservoirs. Two limiting factors are: depth(less than 150 metres) and reservoir thickness(greater than 3.5 metres). The depth limitation is imposed by the critical pressure of steam which is about 3202 psia. Other reservoir parameters beneficial to steam injection are as follows[15];

1. Oil gravity above 12°API
2. Oil viscosities between 100 - 100, 000 centi poise at reservoir temperature
3. Permeability above 50 md
4. Porosity above 25%

These parameters are usually considered as guidelines. Steam and water are excellent heat carriers, but the heat content of a unit mass of steam is much higher than that of water at the same temperature and pressure. Also when the relative permeability of steam is considered, there are instances when water is a better carrier than steam on a volumetric basis. But for a given amount of heat, steam introduces much less water into the formation[15]. As a result, less water is produced with the oil, and this results in the maintenance of more heat in the formation. From these advantages, steam-based methods account for over 70 percent of the world's enhanced oil recovery production.[1,2,4,15].

Their application to reservoirs having low gravity, high viscosity and high porosity have become almost routine[1,14,15]. There is every indication that this segment of enhanced oil technology will continue to grow provided there is adequate supply of water. The United States of America accounts for the highest number of steam injection wells in the world, followed by Venezuala and Canada[15].

In Alberta, the two broad classes of steam based in-situ enhanced oil recovery methods usually used to increase the production rate and ultimate recovery of the heavy oil are Steamflooding and Cyclic Steam Stimulation. Cyclic Steam Stimulation is used for most of the heavy oil recovery in this province. An estimation of expected oil production rate after steaming(Q_{hot} Bbls/day) can be made by the following simple relation[1,15].

$$Q_{hot} = Q_{cold} \frac{\text{Viscosity of oil before steaming}}{\text{Viscosity of oil after steaming}}$$

However, predictions of reservoir response and oil-steam ratio require model studies. In-situ combustion is also used in the production of heavy oil to a smaller extent in Alberta. This technique also adds to the water which eventually goes to waste disposal or recycling.

2.2.1.1 STEAM STIMULATION

This thermal recovery method is also known as: cyclic steam injection, steam soak or huff and puff.[1,2, 14,15] The process involves the injection of 5000 - 15000 barrels of 80 percent quality steam into a producing well for a specified period of time at temperatures of up to 300°C possibly with additives such as gases, surfactants or solvents[1,2,14,15].

Following this , the well is shut-in for a few days to allow sufficient heat dissipation and then placed on production. Heat from the injected steam increases the reservoir temperature, resulting in pronounced increase in mobility of heavy fluids and a corresponding improvement in producing rates. Mixing of the condensed steam with the formation water and reaction with the minerals in the reservoir modifies the composition of the produced fluids.

This thermal recovery method has gained a worldwide acceptance because of early pay out results from successful applications. This technique is primarily a stimulation method, and is schematically illustrated in Figure 4. Many operators, after the application of several steam cycles, usually convert to steam flooding project.

2.2.1.2 STEAM FLOODING

Steam flooding is a thermal recovery process very similar to steam stimulation. First a suitable well pattern is chosen and steam is injected into a number of wells while the oil is produced from other wells. Ideally, injected steam forms a steam saturated zone around the injection well. This is shown in Figure 5. The temperature of the steam zone is nearly equal to that of the injected steam. As the steam moves away from the well, its temperature drops as it continues to expand in response to pressure drop[1,14,15]. At some distance from the well, which mainly depends on the initial temperature of the steam and rate of pressure change with distance from the well, the steam condenses and forms a hot water bank. In the steam zone, oil is displaced by steam distillation and gas in a steam drive. Also in the hot water zone , physical changes in the characteristics of the oil reservoir rock take place and result in oil recovery.

These changes are: thermal expansion of the oil, reduction of viscosities and reduction of viscosity and residual saturation and changes in relative permeabilities[1,15].

2.2.1.3. IN-SITU COMBUSTION

The in situ combustion process[1,14,15] is quite complex as illustrated in Figure 2.6. The reservoir is ignited close to an air /water injection and the combustion front moves away from the well. Behind the combustion front is the post burn zone consisting of sand and residual coke. In the burn zone, the reaction between air and fuel produces mainly carbon dioxide, water, and minor sulphur dioxide; temperatures in excess of 700°C can be reached where breakdown of many of the clay minerals occurs. The high temperatures created by transport of heat ahead of the burn zone causes cracking of the hydrocarbons in the coking /vaporization zone[1,14,15].

The volatiles formed by the cracking move ahead into the steam zone while the residual material left behind is coke, the fuel for the burn. The size of the steam zone depends on the mass of the water injected. The water/steam ratio increases continuously until the water zone is reached where all the steam has condensed. The water zone contains injected water , formation water and water produced by the oxidation of the oil. Oil saturation is increased in the adjacent oil zone because of displacement of oil from the water zone[1,2,14,15]. Finally the preburn zone abuts against the oil zone. These zones sweep out toward the production well as the burn progresses. Consequently, changes in the composition of the produced fluids with time would be expected.

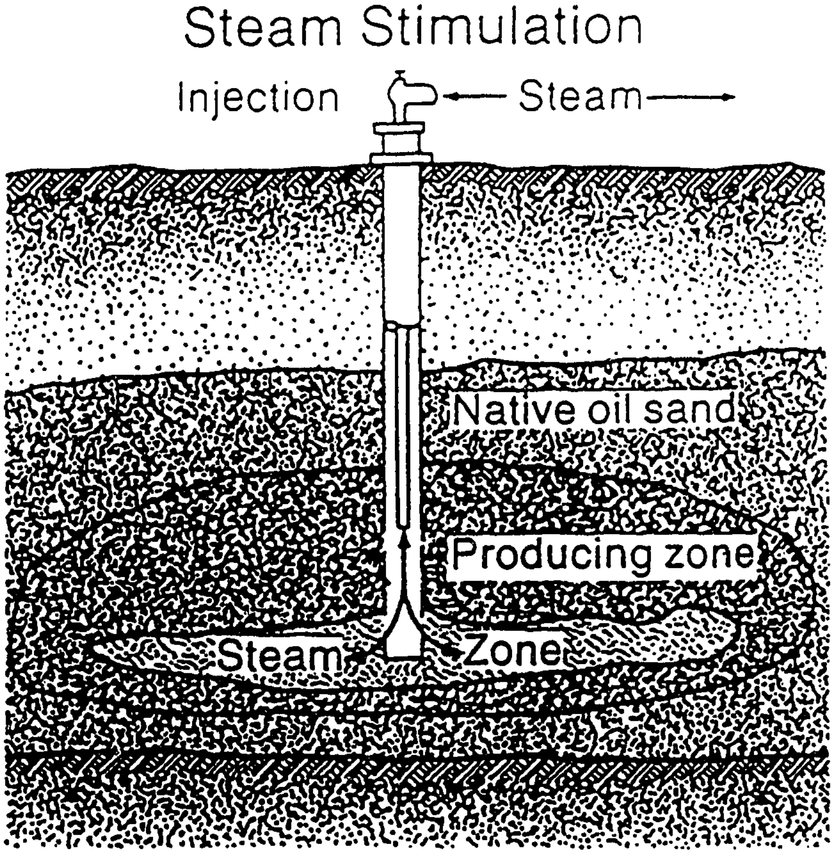


Figure 4. Thermal Recovery; A Schematic Diagram of Steam Stimulation

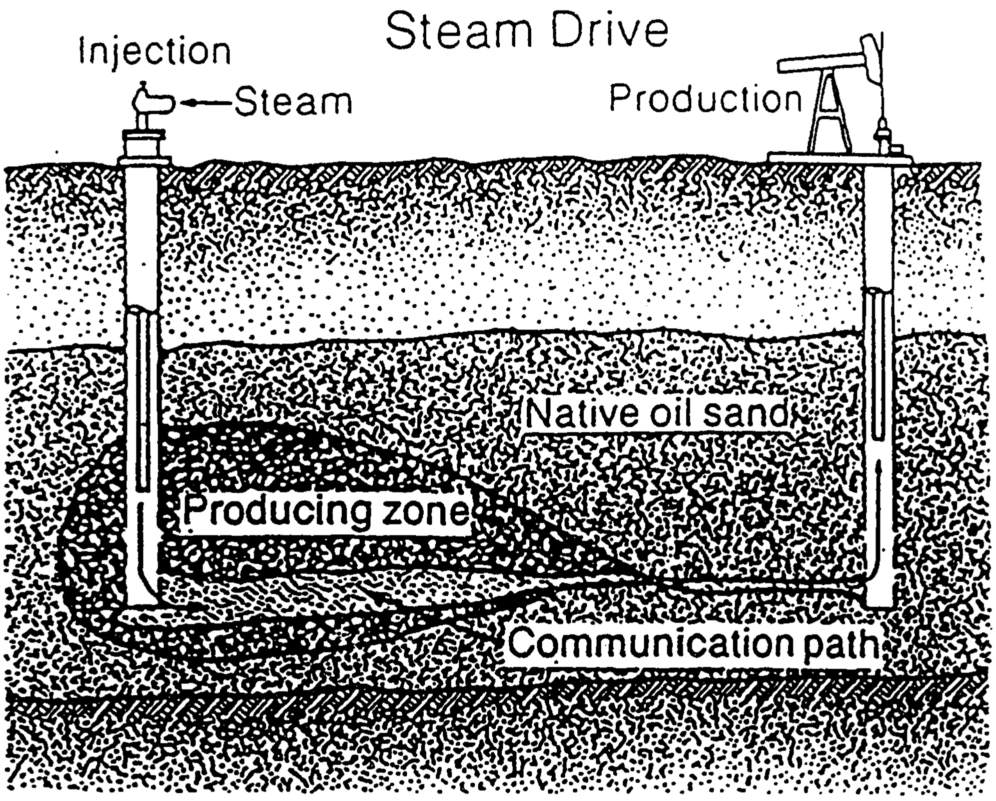


Figure 5. Thermal Recovery; A Schematic Diagram of Steamflood

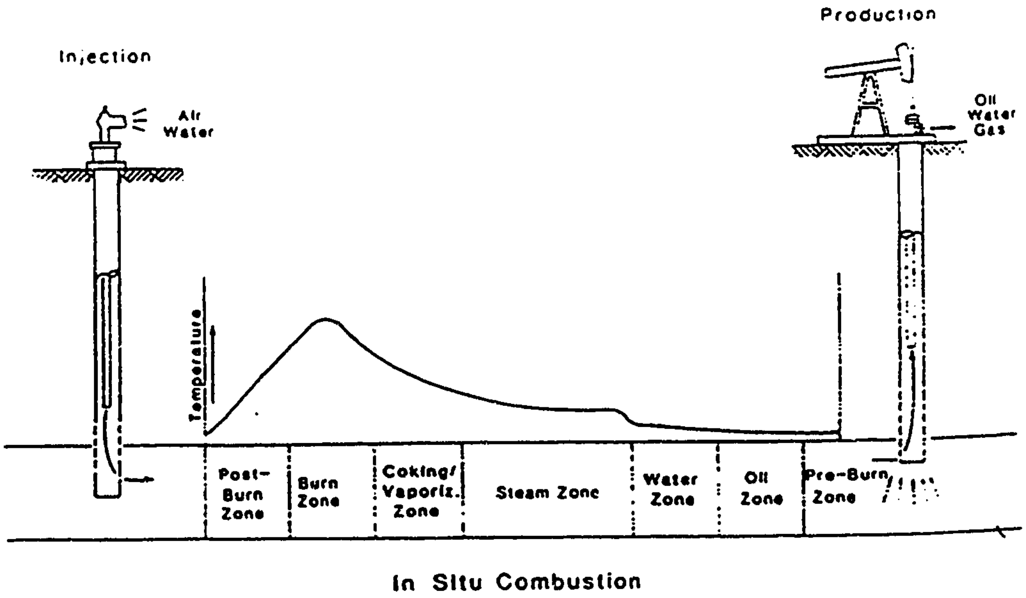


Figure 6. Thermal Recovery; A Schematic Diagram of In-Situ Combustion Zones in a FireFlood

2.3 PRODUCED FLUIDS SEPARATION

The produced fluids consists of crude bitumen, water, sand and other inerts. It is pumped from the producing wells to the surface treatment facilities which are schematically shown in Figures 7 and 8. The produced fluids enter the freewater knockout (FWKO) tank, where the sand and most of the water separates by gravity from the oil phase[11]. Further separation of the water and oil is accomplished in the pressure treater after preheating. Emulsion breakers are applied to facilitate separation. The mixture then goes into an evaporator where further removal of the water occurs. The final product, having a specification of 0.5 percent basic sediment and water(BSW), is then fed into a sales oil storage tank. The sand/water mixture drawn off the FWKO tank is passed through a skim/desand tank via cyclones. The water, called the produced water is then fed into the produced water skim tank. From this skim tank, the produced water, is fed to a wemco induced gas flotation unit(IGF), which is usually operated with a methane blanket at a pressure range of 1.0 - 2.2 kPa[14,15]. The oil /water mixture collected in the launder trough of the IGF is sent back to the skim/desand tank. After the IGF, the produced water passes through a hydromation deep bed filter for additional oil and suspended materials removal.

The effluent from the hydromation unit goes to a disposal tank for further treatment ,recycling or disposal into deep bed. Studies have shown that, suspended oil in the produced water interfere with the treatment of the produce water for recycling, hence suspended oil must be preferably less than 5 mg/l in the produced water. The produced fluids usually have temperatures of about 82 °C and so the final produced water from the separation process also has temperatures in the range of 80°C to 85°C[1,14,15].

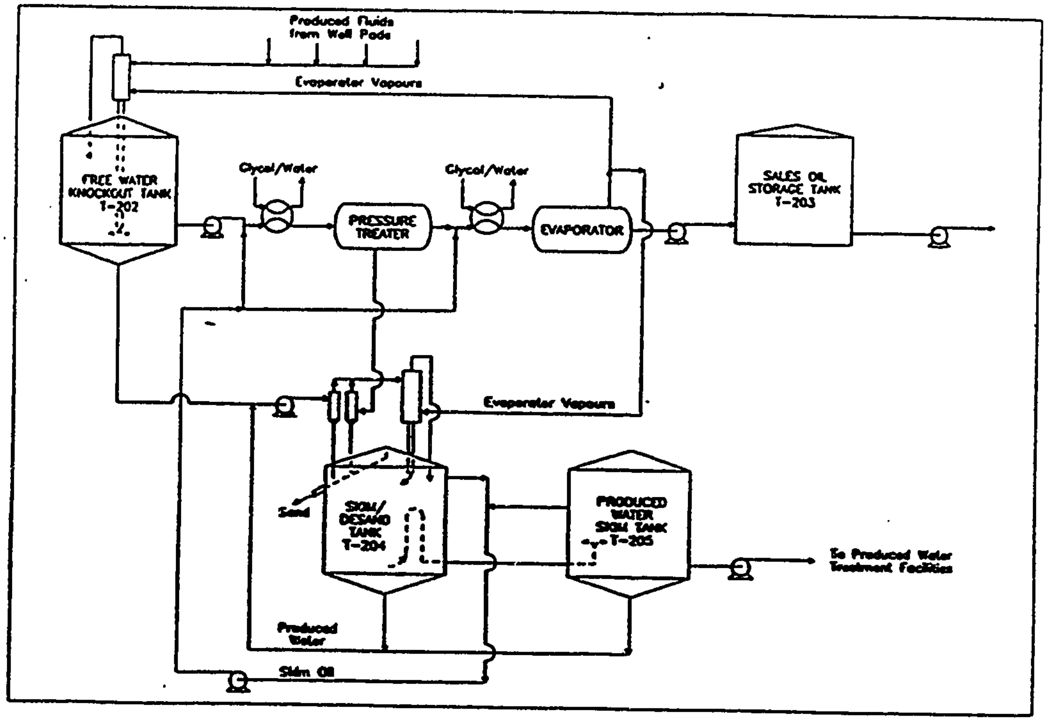


Figure 7. Process Flow Schematic of Produced Fluids Dehydration

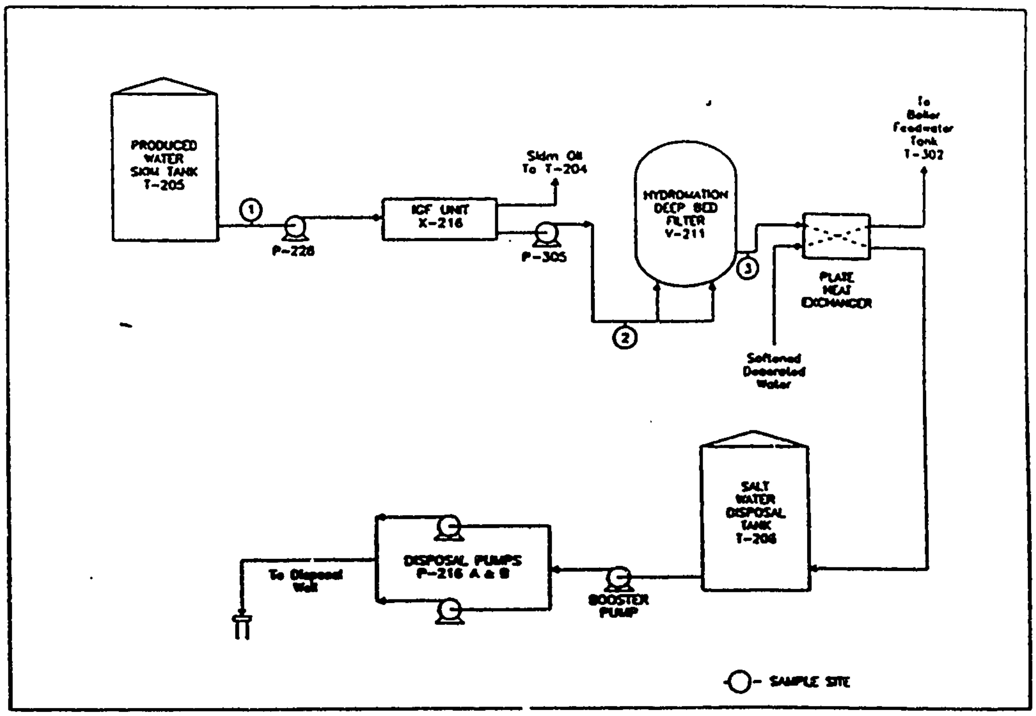


Figure 8. Process Flow Schematic for Produced Water Treatment and Disposal.

2.4. THE PRODUCED WATER PROBLEM

In Alberta , heavy oil production is mainly achieved by steam based in-situ enhanced oil recovery operation which require large quantities of dependable water source that is suitable for steamer feedwater. Operators estimates indicate that current heavy oil production of 100, 000 barrels per day(bpd) is expected to rise to above 500,000 bpd within the next decade[4,9,10,14]. The fresh water requirements in heavy oil production are mainly for steam generation, production inlet cooling and various utility functions. During in-situ production, the required steam - to - oil ratio (SOR) can vary from 2:1 to 20:1, depending on the reservoir characteristics. However, an average SOR of 5:1 is generally indicated in Alberta. This means that, at a heavy oil production rate of 500,000 bpd, at least 2 million barrels or 320, 000 m^3 of water is needed per day. In addition to placing heavy demands on fresh water resources, this level of water usage creates massive wastewater problems, as most of the injected steam is coproduced with oily, ion rich, and silty waters.

Traditional thinking has focused on minimal treatment before injection into salt-water disposal wells(SWD) to some deep formations. Although this practice has some obvious economic advantages, it is no longer accepted in areas like California(U.S.A) where water is a scarce resource[4,9,10]. In Alberta, several producers still utilize SWD but the clear trend has been to recycle produced water for use as boiler(steam generators) feedwaters[4]. A deep SWD well may cost one million dollars, and problems may be encountered with scaling and plugging in the tubing. Produced water recycling offers a reduction in fresh water demands, and the volume of waste water for deep well disposal . Also it allows the producer to have at hand a reliable source of feedwater, an important consideration where supplies are limited.

The reuse of produced waters for steam generation has been in practice since the early 1960's in California[1,2,15]. Within Alberta, Esso Resources conducted the first recycling pilot test at Cold Lake in 1978[15]. Other commercial in situ operations have since initiated some form of produced water treatment, however, it is still the Esso facilities at Cold Lake which currently apply the most extensive recycle operations.

A requirement for operators to maximize recycle of produced water is embodied in Alberta's long- term management plans for in situ oil sands facilities in Alberta[4,14] This is apparent from the recently released,"Water Recycle Guidelines", by the Energy Resources Conservation Board and Alberta Environment (ERCB 1989)[4]. Therefore, in order to meet these water recycling guidelines, it is imperative for each project operator to understand the limitations of oilfield water treatment unit process equipment as they relate to each produced water quality parameter.

2.5 PRODUCED WATER CHARACTERISTICS AND BOILER OPERATION

Produced water contains a wide variety of impurities. These impurities are due to the dissolution of inorganic rock minerals in the injected steam. Furthermore, the composition of the produced waste water depends not only on the modifications that take place during its passage through the reservoir but also on the source water used in the injection well and the water treatment that is carried out in the surface facilities. These produced water impurities are mainly total dissolved solids(TDS), suspended solids, sulphide, oil (dissolved organics), cations, acids and most importantly, dissolved silica and silicates.

These impurities preclude the use of produced water as a direct feedwater to boilers and once - through generators without pretreatment. Table 2 presents typical produced water composition from three in-situ production wells in Alberta in terms of TDS, silica, and iron content. Table 3 also shows the recommended tolerance limits for boiler operating pressures in terms of TDS, alkalinity, and silica concentration in feedwater. Since solubilities are inverse functions of pressure, the tolerance limits for TDS and dissolved silica in once-through boilers will depend on operating pressures of the boilers. Hence, boilers operating at higher pressures can tolerate lower levels of silica and TDS. Silica solubility is also influenced by alkalinity.

The generally accepted limits for once-through steam generators used for in-situ recovery process in Alberta include dissolved silica of less than 50 mg/l and TDS below 8000 mg/l. From Table 2 it is obvious that, all the produced water will have to be treated for TDS and/or silica removal before recycling to the boilers. Techniques for the removal of suspended solids, oil, and hardness from produced water are reported in the literature. However, the data on silica precipitation is the least understood. It is therefore the most expensive in terms of treatment. A description of the contaminants found in produced water, their effects on steam generators and some possible treatment processes follows:

2.5.1 Hardness

The main cause of hardness in water is dissolved magnesium and calcium ions. The salts and oxides of these ions can contribute to corrosion and scale formation in the steam generator's water tubes, resulting in decreased heat transfer (lower efficiency), increased maintenance costs and potential tube failure.

It is generally agreed that conventional once-through generators require feedwater with essentially zero hardness[2,10,16]. If the total hardness in the untreated water is less than 200 to 300 mg/l, then it may be economically removed by ion exchange alone[2]. For hardness concentration of up to 3000 mg/l, hot or cold lime softening upstream of the ion exchange process may economical. If the water contains concentrations which are greater than 3000 mg/l of total dissolved solids(TDS), then several design consideration are required[2,9]. High TDS concentrations substantially increase the hardness leakage from both the lime softeners and from conventional strong acid ion exchange resins.

Hardness observed in Alberta produced water is generally less than 200 mg/liter, hence ion exchange polishing is adequate for removal.

2.5.2 Iron

The iron content of the feedwater should generally be less than 0.05 mg/l. It has been shown that iron will attack the protective magnetite iron oxide layers of boilers[]. The ion exchange systems used for hardness removal are also effective for iron removal. However, iron can cause resin fouling and can catalyze the chemical breakdown of the resin structure. Therefore, if significant concentrations of iron are present, then lime softening should also be considered for iron removal in conjunction with hardness reduction.

TABLE 2

PRODUCED WATER COMPOSITION FROM THREE IN-SITU PRODUCTION WELLS IN ALBERTA

Parameter (mg/L)	Amoco (Lindberg Area)	Shell (Peace River)	Esso (Cold Lake)	AOSTRA UTF Site
TDS	52,000	3,000	8.500	4,700
Silica	32	274	240	239
Iron	0.6	0.1	0.5	0

TABLE 3

TOLERANCE LIMITS OF DISSOLVED SILICA, ALKALINITY AND TDS AS A FUNCTION OF OPERATING PRESSURE

Boiler Operating Pressure (psig)	TDS Limit (mg/L)	Alkalinity (mg/L)	Silica (mg/L)
0-300	3500	700	125
301-450	3000	600	90
451-600	2500	500	50
601-750	2000	400	35
751-900	1500	300	20
901-1000	1250	250	8
1001-1500	1000	200	2.5
1501-2000	750	150	1.0

2.5.3 Oil

All feedwaters should be essentially free of oil before entering the steam generator system. Oil can leave organic deposits on the tubes and lead to corrosion and/ or coking. Assuming that the feedwaters are softened by an ion exchange system, the oil must be removed prior to this system to prevent fouling of the ion exchange resins.

In addition, oils or other organics in the feedwater if allowed to accumulate,can lead to the growth of additional organic matter in tanks and piping system[2,7]. If significant piping distribution system or tankage exist, routine procedures may have to include chlorination for biological control. Residual chlorine must be removed, however, prior to passing the water through an ion exchange system because of the detrimental effect of free chlorine on ion exchange resins[7].

2.5.4 Hydrogen Sulphide

Feedwater for steam generators should also be free of hydrogen sulphide. Sulphide in the feedwater can lead to extensive corrosion of the steam generator tubing. Sulphide in the feedwaters is a common problem, but the general practice is to oxidize the sulphides to sulphates, either chemically or by utilizing an air flotation oil removal system that is open, or partially open, to the atmosphere[29,31].

2.5.5 pH

The pH of the feedwater to the steam generator should be alkaline. It is reported to be approximately 8.0 to 8.5[29,32]. This helps not only to reduce the corrosion between the softened water supply and the steam generator but also will tend to keep silica in solution in the generator.

2.5.6 Suspended Solid(Turbidity)

Turbidity of the water being fed to the steam generators should be essentially "zero".which means that there should be practically no suspended solids. A softening system in the pretreatment train will remove a significant amount of turbidity in the feedwater[7,10]. However, the ion exchange resins may be more prone to fouling if used as a filter. Thus, if the influent turbidity is very high, then traditional coagulation and clarification followed by mixed media filtration prior to ion exchange , may be applicable.

2.5.7 Alkalinity

High alkalinity in multi-circuit utility boiler system is a serious problem. As the temperature and pressure of the feedwater is increased, the carbonate and bicarbonate (alkalinity) in the water tends to break down to form free carbon dioxide and sodium hydroxide. Free carbon dioxide then mixes with the dry steam, but will eventually redissolve when that steam is condensed in a condenser or in the steam lines.

When the carbon dioxide dissolves in this water, carbonic acid is formed which is very corrosive to steel lines[2,7,14]. Softened water alkalinities in excess of 300 mg/l have been routinely fed to the once-through steam generators. However, due to the break down of this alkalinity in the boiler system, the alkalinity of the steam generator blowdown or 20 percent water fraction is essentially zero, as most steam generators are operated at 80 percent quality steam. The corrosive action of carbon dioxide can be prevented as reported in the literature by a filming amine.

2.5.8 Oxygen

Oxygen in the feedwater water can lead to corrosion of the feedwater piping, promoting iron pickup from the steel piping, which attacks the magnetite layer of the steam generator tubes. The oxygen content of the feedwater must be reduced to zero prior to entering the once-Through steam generator. Oxygen can be removed by mechanical or chemical deaeration, followed by chemical polishing[2,14].

2.5.9 Silica and Silicates

Dissolved silica and silicates represent the most important problem in produced water treatment. Silica produces scaling of boiler tubes, both directly and as a constituent of complex minerals scales with the oxides of iron, aluminium, magnesium and calcium. It contributes to caustic embrittlement and produces sludges that can plug the injection pipes[6,7,10]. Several methods are available to control and treat scale formation.

Blowdown is an effective method to remove solids already in the boiler, but this practice represents an economic loss in terms of equipment downtime and wasted heat[7]. Ethylenediamenetetracetic acid may be circulated through the tubes, but this involve shutting down the generator. Thus the method to control this scaling problem is to remove silica before entering the boiler steam generators[3,7,10]. The produced water generated in most Canadian enhanced oil recovery facilities is presently not treated, and cannot be recycled to once-through steam generators.

However, Esso Petroleum Canada has applied the hot lime softening (HLS),process, at temperatures of 80 - 90 °C, to treat produced water from their Cold Lake operations in Alberta for TDS and silica removal. In this process, calcium, magnesium, and silica are partially removed by initially reacting the waste water with hydrated lime.[4,14,15] for hardness removal followed by the addition of magnesia for silica precipitation. The HLS process is schematically shown by Figure 9

The following chemical equations illustrate the HLS process chemistry.

$$Ca(OH)_2(s) \Longrightarrow Ca^{2+}(aq) + 2OH^- \text{ ---------------------------- } \tag{1}$$

$$Mg^{2+}(aq) + 2OH^- \Longrightarrow Mg(OH)_2(s) \tag{2}$$

$$2HCO_3^-(aq) + 2OH^-(aq) \Longrightarrow 2CO_3^{2-}(aq) + 2H_2O(l) \text{ -} \tag{3}$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \Longrightarrow CaCO_3(s) \text{ --} \tag{4}$$

The main reaction products are $CaCO_3(s)$ and $Mg(OH)_2(s)$. The mechanism of removal of silica by magnesia and the precipitating compounds is not known. There are presently two main theories which have been proposed to explain the silica removal step. These are the surface adsorption theory, and the complex formation theory[16,17].

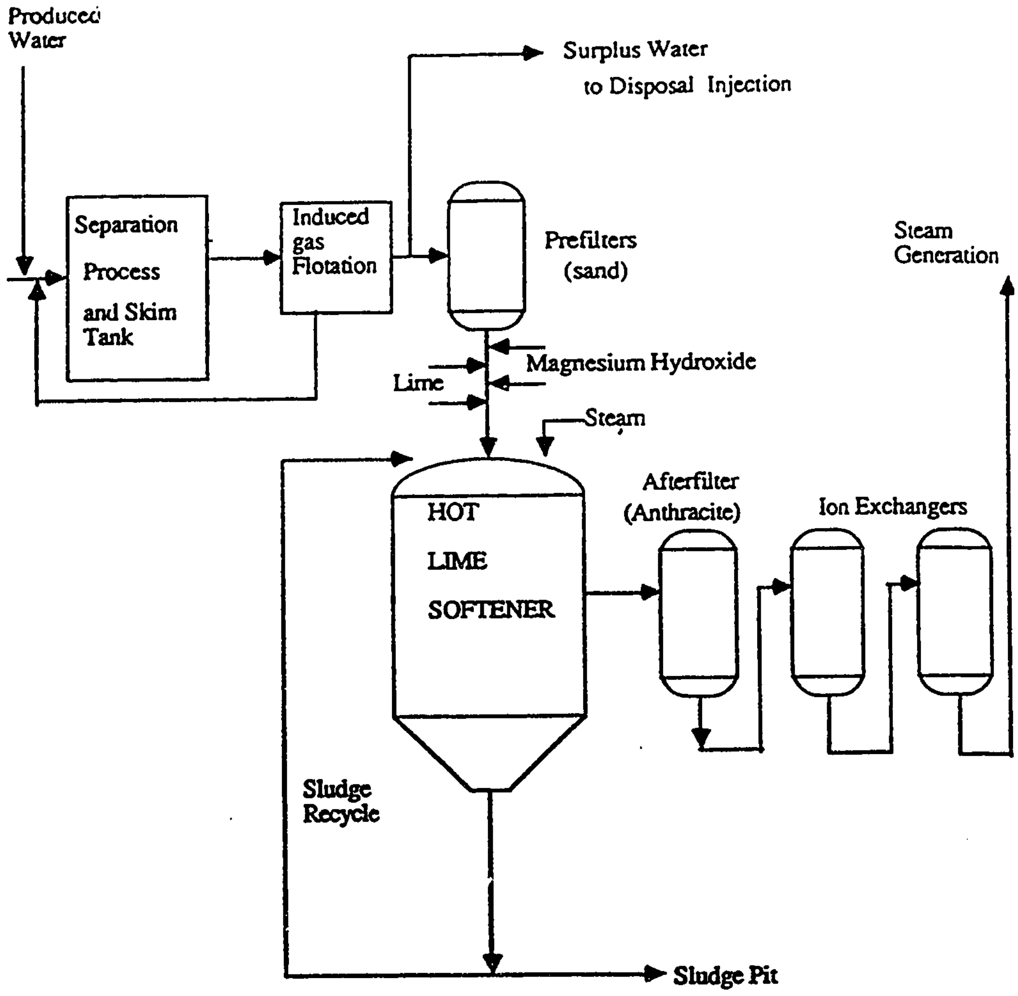


Figure 9. A Schematic Diagram of Produced Water Treatment by Hot Lime Softening Process (HLS)

proposed the formation of a solid solution of magnesium silicate hydroxide of the general form $Mg(SiO_4)_x(OH)_{2-x}$. These complex silicate salts can behave as gelling agents which can precipitate as sludge. Other researchers such as Applebaum have proposed that silica is simply adsorbed onto the surface of the precipitating magnesium hydroxide and calcium carbonate[7]. Historically, the softener performance for removing silica has been modeled using the Fruendlich adsorption isotherm model. Both ionic and solid magnesium additives have been used in laboratory jar tests and the data fitted to the Freundlich isotherm[17]. However, Muriego used a kinetic model to predict silica removal based upon the formation of a magnesium silicate (sepiolite)[17]. He also showed that a mathematical expression of the same general form as the Fruendlich isotherm could be derived and used to describe a magnesium silicate precipitate reaction. However industrial application of the HLS process has revealed a number of serious problems. Some of these problems include:

(1) High capital and operational costs.

(2) Production of large quantities of highly toxic alkaline sludge, which makes it environmentally hazardous to use conventional solid waste disposal methods such as land fill.

The seriousness of the problems associated with the HLS process have resulted in the search for alternative treatment methods. A promising alternative technology involve silica removal by the hydrogarnet method. This technique has been successfully used for the removal of dissolved silica from aqueous aluminate solutions. Hydrogarnet is a member of a group of compounds, called garnets, which are complex hydrated calcium aluminium silicates[12].

The desiliconization process using the hydrogarnet method has been applied in the production of high grade aluminium hydroxide solution but not in produced water treatment. It consist of the conversion of dissolved silica and silicates in aqueous solutions into a stable and filterable precipitate such as calcium aluminosilicates[8].

2.5.10 **Silica Removal by the Hydrogarnet Process**

The first step in this desiliconization process is the production of tricalcium hydroaluminate, which is formed by the reaction of $Ca(OH)_2$ and $Al(OH)_3$. The reaction may be expressed as

:

$$3Ca^{2+} + 2Al(OH)_4^- + 4OH^- \Longrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O \text{ ----------------(5)}$$

The tricalcium hydroaluminate is then used to effect the desiliconization step by reacting it with the solution containing the silicate ions. A stable insoluble tricalcium aluminosilicate precipitate, known as hyrogarnet, is formed according to the following reaction

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + nSiO_3^{2} \Longrightarrow 3CaO \cdot Al_2O_3 \cdot nSiO_2 \cdot (6\text{-}2)H_2O + 2nOH^- + nH_2O \text{ ------------------------(6)}$$

The stable hydrogarnet compound containing most of the silica can be removed by filtration and disposed in unprotected landfills. The lack of a constant stoichiometric coefficient (n) for the silicate ion, raises some problems in carrying out the reaction balance[8].

The value of (n) however depends on the activity of the tricalcium hydroaluminate and the method of preparation. For an Al_2O_3 - SiO_2 - CaO system, the equilibrium for reaction (6) lies towards the hydrogarnet so that the equilibrium concentration of silicate ions in solution approaches zero. If the solution of silicate ions also contains some carbonate ions, some of the tricalcium hydroaluminate may dissolve according to reaction (7) to form $CaCO_3$.

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaO_3^{2-} \Longleftrightarrow 3CaCO_3 + 2Al(OH)_4^- + 4OH^- \text{ ------------ } (7)$$

Hence sufficient hydroaluminate must be added to ensure complete desiliconization in the presence of carbonate anions. It is believed that the desiliconization reaction (6) is a surface reaction where the initial step involves the adsorption of silicate ions on the surface of the tricalcium hydroaluminate[8].

Subsequently, the adsorbed silicate ions are incorporated into the hydroaluminate lattice to form a combination of hydrogarnet type compounds, which in turn activates further silicate fixation in an autocatalytic reaction. Furthermore, when reaction (6) occurs, the pH of the solution increases due to the release of OH^- ions. The OH^- ions released can react with other cations, particularly Mg^{2+}, to form hydroxide precipitates, thereby further reducing the dissolved cations. The increase in the treated water pH may also be advantageous in recycling the desiliconized solution for steam generation. This desiliconization reaction can be carried out over a wide range of temperatures from 15°- 90°C.

2.5.11 Total Dissolved Solids (TDS)

TDS can cause severe scaling problems in the boiler-steam generator system, and hence, reducing the efficiency of the system. It also causes caustic embrittlement in boilers and severe plugging problems in injection pipes. Blowdown can be used to control this problem, but economically it is not feasible as described above in the case of silica. Technologies designed specifically for TDS removal from produced water do not exist. However, a considerable amount of data is available on TDS removal technologies from sea water (TDS = 35 ,000 mg/L) and brackish water (TDS = 5000 - 10000 mg/L) for drinking water production[11].

The TDS concentration of seawater is generally in the range of TDS concentration for high TDS produced water (25 ,000 - 100,000 mg/L). Therefore, the process used for seawater desalination may be applicable to some produced water treatment. However, several differences exist between produced water and seawater. For example, produced water generally has higher concentrations of oil and grease, silica, dissolved organics, hardness, and lower sulphate concentrations than seawater. Some of the technologies which have been identified for TDS removal from seawater and brackish water include; ion exchange, membrane separation by reverse osmosis, and vapour compression evaporation (VCE) [11]. The VCE process for TDS removal from produced water has been studied at a pilot scale by Environment Canada's Wastewater Technology Centre (WTC) in collaboration with Alberta Oil Sands Technology and Research Authority (AOSTRA) and several oil companies[11]. The conclusion from the pilot plant study was that VCE will require very high capital and operating costs in the tens of millions of dollars, and its effectiveness at high TDS levels is doubtful as VCE also results in the production of toxic sludge as by-products which must be disposed of in deep salt wells. Such disposals also represent a potential environmental problem due to the possibility of ground water contamination.

2.6 ENVIRONMENTAL EFFECTS OF PRODUCED WATER DISPOSAL

The produced waters from Alberta heavy oil and tar sands development operations contains high salinity (NaCl), total dissolved solids, and some amount of oil[4,14,33]. High saline water presents three major ecological problems[33]. It is non-biodegradable ; sodium chloride is mobile and highly toxic to vegetation and sodium acts as a long term soil contaminant. Disposal of produced brine water on forested lands has had devastating effect on vegetation and has severely altered the physico - chemical characteristics of the soil. The high concentration of soluble salts results in a corresponding high osmotic pressure. The impact of produced water on soils is most evident in terms of extractable cations. Following contact with produced water(high Na), the proportion of this ion on the exchangeable complex of the soil increases sharply relative to calcium and magnesium.

Soil with exchangeable sodium in excess of 15 percent is termed as sodic and its structure deteriorates as soil particles are dispersed thus restricting drainage[14,33]. The soil becomes blocky and compact instead of being friable. Hence vegetation is injured or killed because of osmotic and nutrient stress and the uptake of toxic amount of certain constituents such as chloride. There has been the debate that natural forces may presumably be able to heal most of the scars created by produced brine water, given sufficient time. However this may not always happen within the time frame acceptable to the owner of the land. During the last decade there have been various suggestions and warnings that produced water entering the environment may constitute a health hazard to humans since produced water contains a significant amount of deleterious volatile organic compounds. The contact with humans may be acute or chronic.

Humans uptake may be by inhalation,skin contact ,or even by ingestion[19,20,33]. Problems also arise when produced waters are discharged into water bodies. Studies have shown that due to high salinity and temperature of produced water,most aquatic life and food are destroyed when produced waters are discharged into fresh surface waters. Furthermore,the discharge procedure into water bodies renders these waters undrinkable.

Produced waters have mainly been disposed by Salt Water Deep Bed Method[1,4,5,14,29,33]. This method is no more acceptable due to the pollution of underground waters which serve as the main source of water for most farms and industries. Hence reuse of produced water is the best solution to these environmental problems.

3.0 EXPERIMENTAL

3.1 MATERIALS

The three produced water samples used for this study were representative samples obtained from Amoco (Lindberg Area), Shell (Peace River), and Esso (Cold Lake) heavy oil operations. These samples were taken from the effluent of the hydromation unit as described earlier. Since suspended oil in the produced water interferes with precipitation process, it was necessary to ensure that suspended oil in the samples was less than 5 mg/l.

Analytical grade calcium hydroxide {$Ca(OH)_2$} and aluminium hydroxide {$Al(OH)_3$} were used for the preparation of the tricalcium hydroaluminate precursor. Analytical grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) were also used in the acidification and pH adjustment of the Shell produced water sample during decarbonation. The produced water samples had a pungent smell indicating the presence of hydrogen sulphide gas. The water samples were colourless when kept in a cooler but turns to a deep wine colour when left open in the laboratory suggesting the occurrence of a photochemical reaction.

3.2 PRODUCED WATER SAMPLES ANALYSIS

The produced water samples were characterized using standard wastewater chemical analysis procedures. The samples were prepared by removing all the suspended solids by filtration. The filtrate was used as the liquid sample for the various analysis.

3.2.1 pH DETERMINATION

The pH of the produced water samples were obtained by using Canlab pH meter consisting of a glass electrode and a temperature compensating adjustment. The instrument was standardized with a buffer solution of pH 7 and temperature adjusted to the prevailing room temperature. The pH readings were obtained on a digital screen to an accuracy and reproducibility of 0.01 pH unit. During the desiliconization reaction the pH readings were taken continuously without prior filtration.

3.2.2 X- RAY DIFFRACTION ANALYSIS

The powdered diffraction patterns of the TDS residues, tricalcium hydroaluminate precursor, and the desiliconization precipitate were obtained on a Philips PW 1380 Diffractometer equipped with a horizontal goniometer[27]. The solid residues were scanned at 0.5°/min from 10° to 80°C using copper K-alpha radiation and a nickel filter. The diffraction peaks were identified by matching the pattern of the unknown with tabulated patterns. A confirmation of the presence of a particular compound was only made when diffraction pattern matches with a detailed pattern published in the ASTM Powder diffraction file.

3.2.3 SCANNING ELECTRON MICROSCOPY ANALYSIS

The individual total dissolved solids (TDS), tricalcium hydroaluminate precursor, and desiliconization precipitate particles were all viewed by ISI - 60 Scanning Electron

Microscope (SEM) operated at 30 Kev equiped with a Princeton Gamma Tech (PGT) System 4 Energy Dispersive X-Ray Analyzer.(EDA)[]. This equipment was also used to identify constituent elements and compounds with concentration which were too low (below 10 wt. %) to be detected by conventional X-ray diffraction.

3.2.4 INDUCTIVELY COUPLED PLASMA (ICP) ANALYSIS

The various cations (metals) in the produced water samples were obtained by an ICP source consisting of a flowing stream of argon gas ionized by an applied radio frequency field oscillating at 27.1 MHz[]. The samples were purged with HNO_3 and the sample aerosol generated in the pneumatic nebulizer was carried into the plasma through an injector to a spray chamber which subjects the constituent atoms to temperatures of about 6000 to 8000°K. Ionization of a high percentage of the atoms produces ionic emission spectra. This spectra was sequentially examined by a computer controlled read out attached to the polychromator. The cations in the desiliconization filtrate were also obtained by ICP.

3.2.5 FLAME PHOTOMETER ANALYSIS

Sodium ion concentrations of the produced water samples were obtained by flame emission photometry equipment with computer controlled read out at calibrated wavelength. A calibrated curve was obtained by ploting absorbance from the digital readout against standardized sodium ion concentration. The sodium ion concentrations of the produced waters were obtained by matching the corresponding absorbance on the calibrated curve.

2.5 CHEMICAL ANALYSIS

The chloride content of the produced water was analyzed using the SM (4500 Cl . G. DPD) Colorimetric method. With this method, a spectrophotometer providing a light path of 1 cm and a wavelength of 515 nm was calibrated with chlorine water standards in the range of 0.05 to 4 mg/l from 100 mg/l chlorine water standardized as follows: 1 ml of acetic acid was added to 10 to 25 ml chlorine demand free water in a flask. One gram of potassium iodide (KI) and 2 ml of starch were then added to the chlorine solution. The chlorine solution was titrated with 0.025N $Na_2S_2O_3$ solution until the yellow iodine disappeared. The titration was continued to the final disappearance of the blue colour. A blank solution was determined by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample used for the titration. The concentration of the chlorine was determined as follows:

$$\text{mg Cl as } Cl_2\text{/ml} = \frac{(\text{ ml of titrant of sample } + \text{ ml titrant for blank}) \times \text{N of } Na_2S_2O_3 \times 35.45}{\text{ml of sample}}$$

3.3 PREPARATION OF TRICALCIUM HYDROALUMINATE PRECURSOR

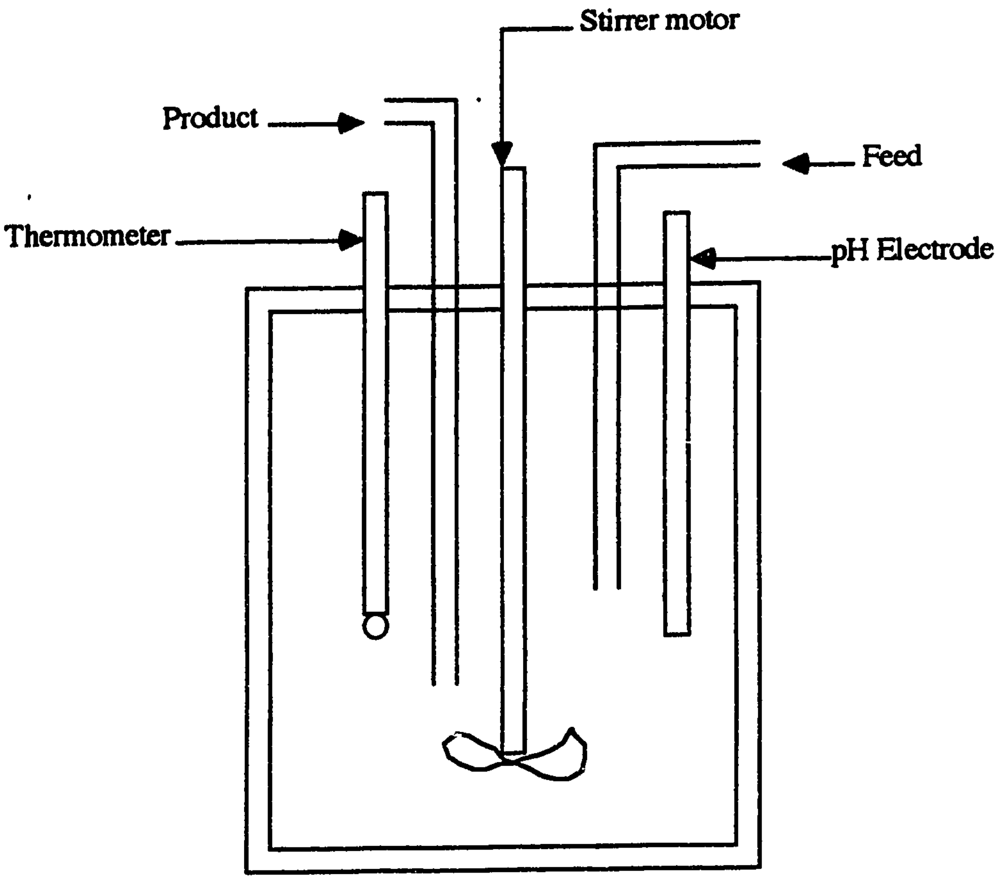
The tricalcium hydroaluminate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$) precursor was prepared by hydrothermal treatment of known amounts of $Ca(OH)_2$ and $Al(OH)_3$ at about 150°C[28,41] and autogeneous pressure (approximately 100 psi) in a stainless steel jacketed 300 ml Parr autoclave equipped with a magnetic stirrer and, a temperature and a pressure gauge.

Typically, a mole ratio of 1.5: 1.0 of $Ca(OH)_2$: $Al(OH)_3$ was charged into a 300 ml autoclave. The temperature was maintained within ±0.1°C of the desired value and 99.9% nitrogen was supplied to the autoclave via dip tube. A known quantity of water was added to the mixture until a water to solid ratio of 15:1 was obtained. The autoclave was sealed and heated electrically to 150°C with continuous stirring. The reaction was continued for one hour. At the end of the reaction period, the autoclave was depressurized via steam release through an injection valve and allowed to cool. The solid tricalcium hydroaluminate product was then filtered by vacuum filtration before drying to a constant weight at 105°C in a vacuum oven. The solid product was finally characterized by x-ray diffraction and SEM to confirm the formation of tricalcium hydroaluminate before using for desiliconization reaction.

This elevated temperature autoclave method was used for the hydroaluminate preparation in order to ensure complete reaction of $Ca(OH)_2$ and $Al(OH)_3$ and to increase the rate of tricalcium hydroaluminate formation. The tricalcium hydroaluminate can also be prepared at ambient temperature and pressure but at a slower rate. Other tricalcium hydroaluminate samples were prepared by changing the mole ratio and the reaction conditions in the autoclave.

3.4 DESILICONIZATION REACTIONS.

The desiliconization reactions were carried out in a teflon laboratory reactor equipped with a continuous variable speed stirrer as shown in Figure 10. The teflon reactor was heated by a water bath positioned on a hot plate. A known amount of the tricalcium hydroaluminate was added to a measured quantity of produced water at the desired reaction temperature.



CUTAWAY VIEW

Figure 10. A Schematic Diagram of Laboratory Reactor of the Desiliconization Reactor Set-up.

Initially 1.3g of the tricalcium hydroaluminate was added to 300 ml (water to precursor ratio of 231:1) of the produced water sample. Desiliconization reactions were subsequently carried out at water to solid ratios of 300, 600 and 900. The desiliconization reaction were also conducted at temperatures of 23°C (296°K), 40°C (313°K),55°C (328°K), and 85°C (358°). During the reaction, 2 ml aliquots were collected at 5 minute interval for 35 minutes before the reaction was stopped. After cooling and filtering, the liquid samples were analyzed for silicon (Si) as silica (SiO_2), calcium (Ca), magnesium (Mg), and in some cases Aluminium (Al) using Inductively Coupled Plasma (ICP) spectroscopy. In addition, some of the liquid samples were analyzed for dissolved sodium ions by means of a flame photometer. The pH of the reacting mixture was monitored throughout the desiliconization process. The solid precipitates recovered after the desiliconization reactions were dried at 105°C and characterized by x-ray diffraction and SEM/EDS analysis in order to determine the precipitated compounds. Similarly, some of the liquid samples obtained after the desiliconization were used for residual TDS determination.

3.4.1. CARBONATES AND BICARBONATES REMOVAL

Due to relatively high carbonate and bicarbonate content, some of the Shell produced water sample, was decarbonated by acidifying with hydrochloric acid (HCl) to pH of 2. Nitrogen gas was bubbled through and the pH was subsequently adjusted to 7 by the addition of sodium hydroxide (NaOH). The resulting wastewater sample was then used for desiliconization reaction. This pretreated water was designated as decarbonated water-1. Decarbonation by weakly acidic ion-exchange was also investigated for comparison with decarbonation by acidifcation in terms of silica removal. About 250 ml of Shell produced water was passed through an ion exchange column with a total resin volume of 140 cm^3 at a constant rate of 120 ml per hour. A pH of 2 was used as an indicator for the collection of the resultant water which was purged with nitrogen gas for the removal of excess carbon dioxide gas. The pH of the water was finally adjusted to 7 by addition of NaOH and used for desiliconization. This pretreated water was designated as decarbonated water-2.

3.5 WEAKLY ACIDIC ION EXCHANGE POLISHING

In order to remove residual cations, e.g Ca, Mg, and Al from the desiliconized produced water, a weakly acidic ion exchange polishing step was tested. The desiliconized water obtained from the decarbonated water-1 was passed through a hydrogen form weakly acidic ion exchange column with total bed volume of 140 cm^3 at a flow rate of 120 ml/h. During the experiment 5 minutes was allowed for equilibration before the first 10 ml aliquots were taken. 10 ml aliquots were then collected at 5 minutes interval for a period of 2 hrs. The pH was used to determine the arbitrary break-through point of the column. The polished water samples were then analyzed for calcium, magnesium and aluminium ions by ICP Spectroscopy and the sodium ions by Flame photometry. Part of the softened water was also used for TDS determination. Finally, the column was regenerated with 3 M HCl about three times to determine the column efficiency with respect to the operating capacity of the resin.

4.0 RESULTS AND DISCUSSION

4.1. SAMPLE CHARACTERIZATION

The produced water samples were analyzed using various instrumental and chemical analysis as described in the experimental section. The analytical data obtained for the three produced water samples are illustrated in Table 4. The table shows that the Amoco sample contains a very high content of TDS as compared with the shell and Esso samples. The dissolved solids in the Amoco sample are characterized by a high content of sodium, chloride, calcium and magnesium. However, the dissolved silica content in the Amoco water at 32 mg/liter is much lower than the corresponding concentrations in the Shell and Esso samples. The high concentration of ionic species in the Amoco produced water sample resulted in a large interference in the determination of silica in this sample, leading to a high background noise in the ICP spectrum.

Figures 11,12 and 13 present typical ICP spectra for the Amoco, Shell and Esso samples respectively. The Amoco spectrum (Figure 11) shows a large background noise as compared to the Esso and Shell spectra. The background hump completely obscures the silicon peak, thus causing analytical inaccuracies. Since Amoco sample contained mainly TDS, and low concentration of dissolved silica, only the shell and Esso samples were used for further desiliconization studies. All the ICP spectra indicate the presence of Ca, Mg and Si in the produced water samples. Tables 5,6 and 7 show the x-ray diffraction data for the TDS residues from Amoco, Shell and Esso samples respectively. The data indicate that only NaCl, $NaClO_3$ and KCl are detectable by x-ray diffraction in the three TDS residues. The results are in agreement with the chemical analyses data in Table 4 where Na^+,Cl^- and K^+ ions are indicated as the dominant ionic species in the samples.

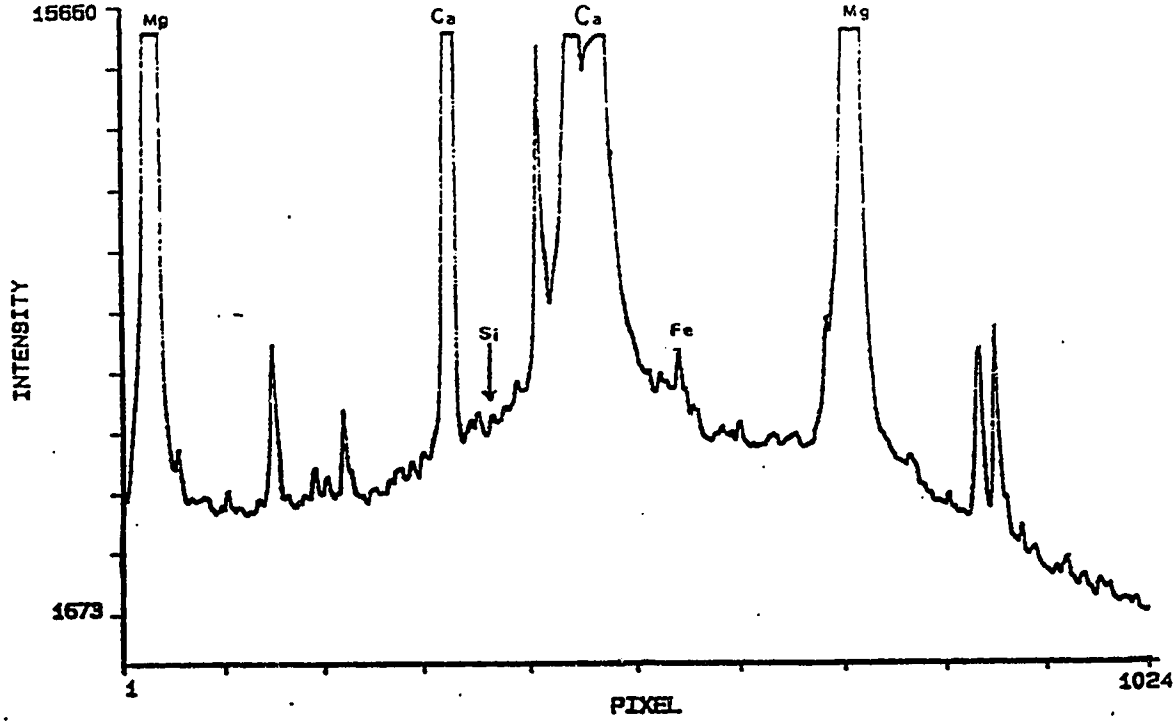


Figure 11. ICP Spectrum of Cation Composition of Amoco (Lindberg) Produced Water Sample

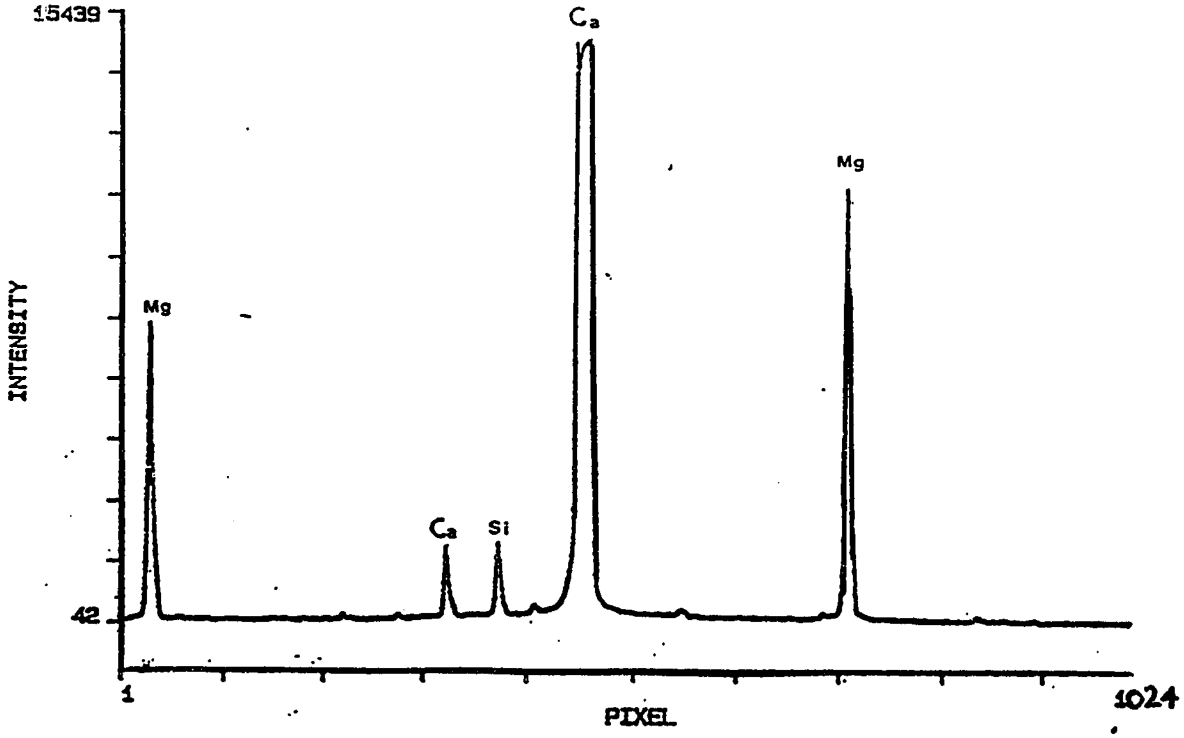


Figure 12. ICP Spectrum of Cation Composition of Shell (Peace River) Produced Water Sample

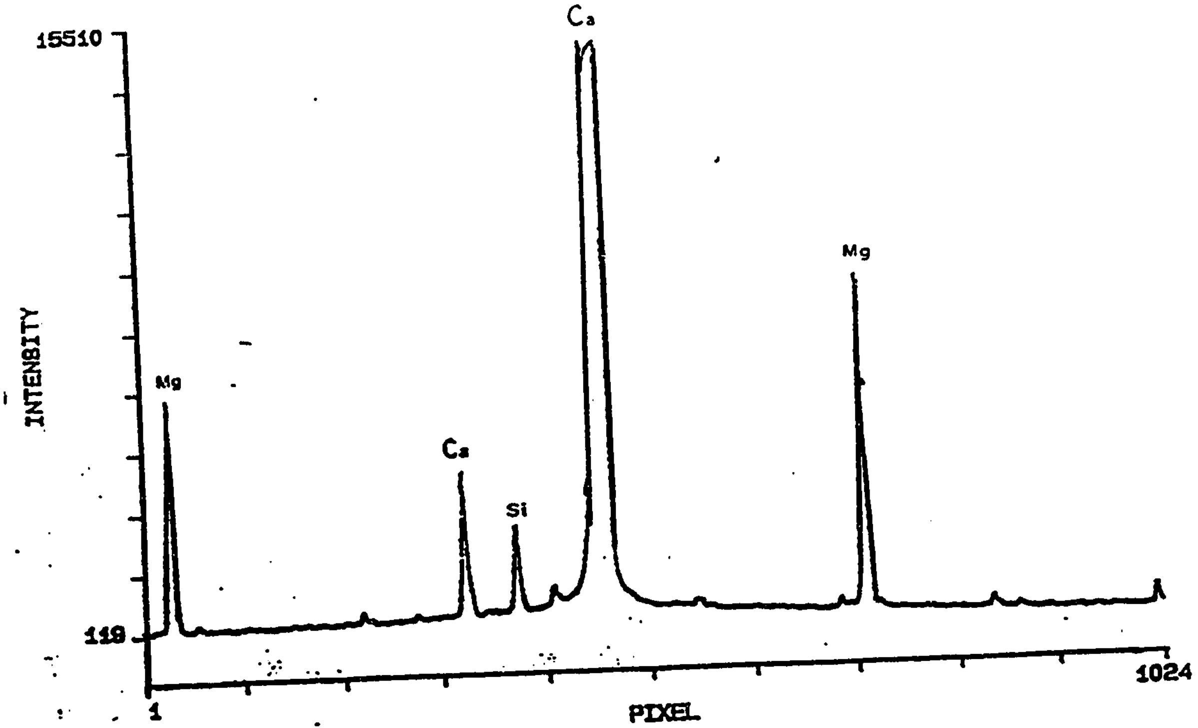


Figure 13. ICP Spectrum of Cation Composition of Esso Produced Water Sample

TABLE 4

CHEMICAL ANALYSIS DATA FOR PRODUCED WATER

Parameter (mg/L)	Amoco (lindberg)	Shell (Peace River)	Esso (Cold Lake)
pH	6.9	7.85	6.95
TDS	52,000	3,000	8,500
Silicon (SiO_2)	32.0	221.96	239.08
Calcium	1,580	33.0	72.7
Magnesium	870.0	7.1	5.8
Sodium	20,500	929.0	2,500.0
Potassium	111.0	929.0	1900.0
Iron	18.1	0.1	0.5
Sulphate	671.0	19.0	ND
Chloride	32,500	929.0	ND
Bicarbonate	102.0	830.0	ND
Nitrate	0.1	ND	ND
Alkalinity	84.0	ND	ND
Hardness($CaCO_3$)	7,310	24.0	ND

ND = Not Determined

TABLE 5

X-RAY DIFFRACTION DATA FOR DISSOLVED SOLIDS RESIDUES FROM AMOCO PRODUCED WATER (Cu Ka Radiation and Ni Filter)

2Ø (deg)	d-spacing (Å)	Rel. Int (%)	Identified Phase
31.9	2.80	100	NaCl
45.6	1.99	100	NaCl
54.0	1.70	11	NaCl
56.7	1.62	66	NaCl
66.3	1.41	22	NaCl
75.3	1.26	88	NaCl
75.6	1.26	93	NaCl
84.2	1.15	19	NaCl
23.2	3.83	18	$NaClO_3$
23.5	3.78	19	$NaClO_3$
23.8	3.74	19	$NaClO_3$
27.0	3.30	21	$NaClO_3$
32.2	2.96	18	$NaClO_3$
32.5	2.93	19	$NaClO_3$

TABLE 6

X-RAY DIFFRACTION DATA FOR DISSOLVED SOLIDS RESIDUES FROM SHELL-PRODUCED WATER (Cu Ka Radiation and Ni Filter)

20 (deg)	d-spacing (Å)	Rel. Int (%)	Identified Phase
27.6	3.23	92	NaCl
31.9	2.88	100	NaCl
54.6	1.70	8	NaCl
56.6	1.62	39	NaCl
66.3	1.41	11	NaCl

TABLE 7

X-RAY DIFFRACTION DATA FOR DISSOLVED SOLIDS RESIDUES FROM ESSO-PRODUCED WATER (Cu Ka Radiation and Ni Filter)

2Ø (deg)	d-spacing (Å)	Rel. Int (%)	Identified Phase
27.4	3.25	20	NaCl
31.9	2.80	100	NaCl
45.8	1.99	77	NaCl
54.0	1.70	12	NaCl
56.8	1.62	28	NaCl
66.4	1.41	71	NaCl
73.1	1.29	5	NaCl
75.5	1.26	28	NaCl
28.5	3.13	18	KCl
40.8	2.21	10	KCl

In general, X-ray diffraction will readily detect compounds with concentration higher than 10 wt % in a composite solid sample. However, EDS spectra of the same TDS residues on a scanning electron microscope, as shown in Figures 14, 15 and 16 for Amoco, Shell and Esso samples respectively, indicate the presence of substantial amounts of calcium and magnesium compounds in addition to sodium , potassium and chlorides. The EDS spectra for TDS residues from Shell and Esso samples as illustrated by Figures 15 and 16 also shows the presence of significant amounts of silicon and sulfur compounds. These silicon and sulfur peaks are not observed in the EDS spectrum of the Amoco TDS residue. The detection of these additional constituents in the TDS residues, relative to X-ray diffraction is due to the better sensitivity of the EDS analysis.

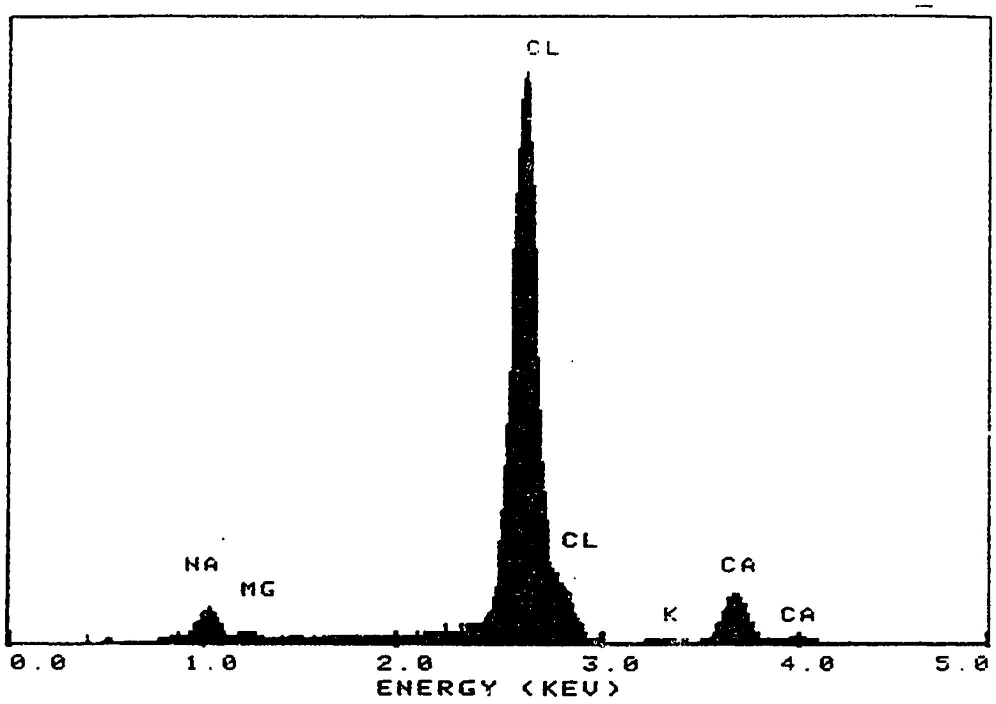


Figure 14. Energy Dispersive X-Ray Spectrum (EDS) of TDS Residue from Amoco Water Sample

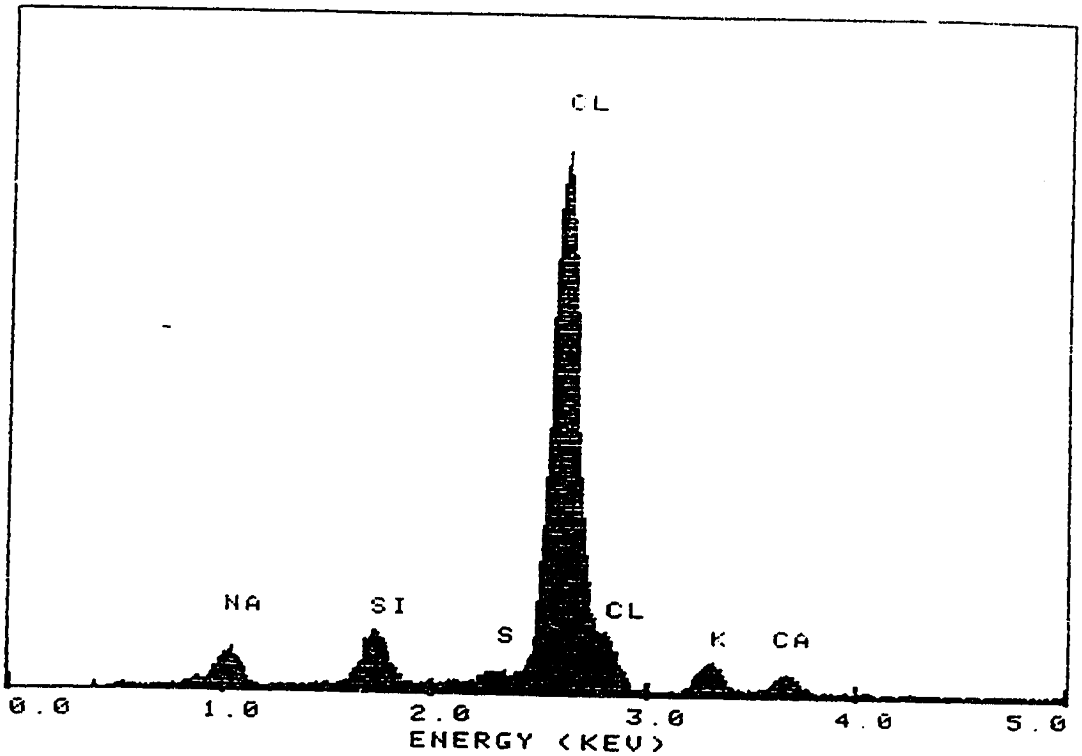


Figure 15. Energy Dispersive X-Ray Spectrum (EDS) of TDS Residue from Shell Water Sample

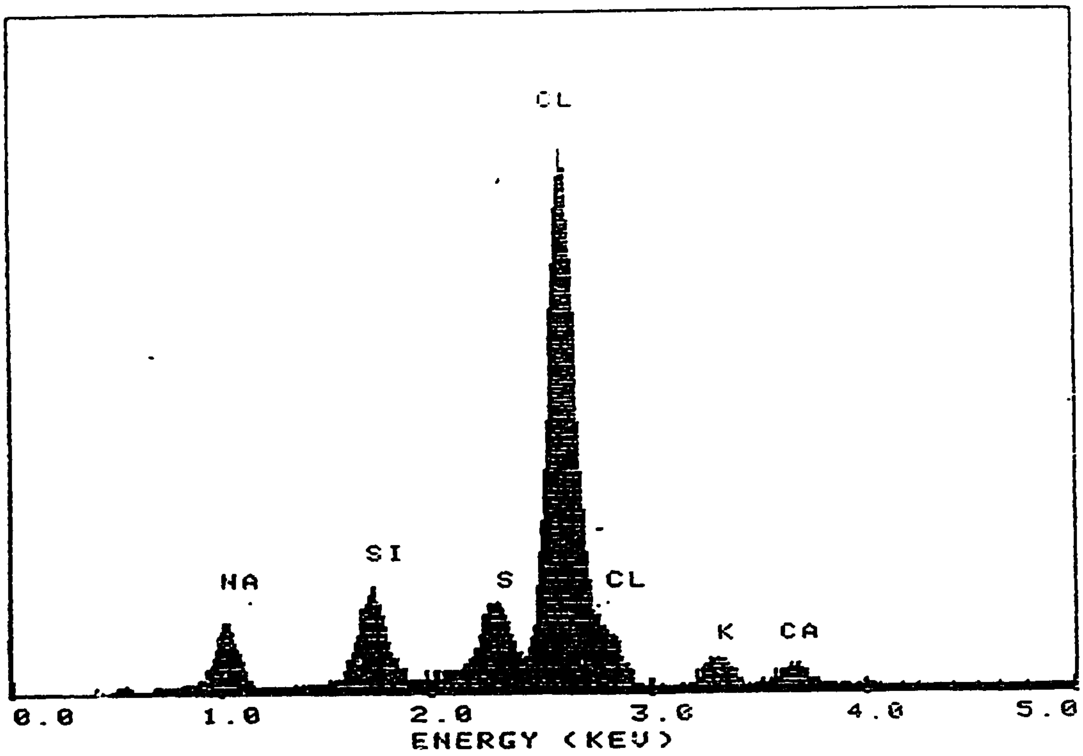


Figure 16. Energy Dispersive X-Ray Spectrum (EDS) of TDS Residue from Esso Water Sample

4.2 TRICALCIUM HYDROALUMINATE PRECURSOR

The x-ray diffraction data obtained for the tricalcium hydroaluminate precursor are presented in Table 8. The data show that only the desired $3CaO. Al_2O_3. 6H_20$ compound is detected, suggesting a complete reaction between the $Ca(OH)_2$ and $Al(OH)_3$ reactants during precursor preparation. This results is confirmed by the EDS spectrum in Figure 18, where only calcium and aluminium peaks are detected. The SEM micrograph of tricalcium hydroaluminate precursor particles (light images) are shown in Plates 1 and 2 at magnifications of 1500 and 3000 respectively.

This SEM electron beam reveals morphological features at the surface and penetrates to a depth of about 5×10^{-3} μm. Information presented by several workers shows that, the tricalcium hydroaluminate crystallizes in the form of cubes and more rarely as dodecahedrons, depending on the method of preparation[26,27,31]. The crystals therefore belong to the normal or holohedral class of the isometric system. Tricalcium hydroaluminate precursor prepared from the hydrothermal treatment of calcium hydroxide {$Ca(OH)_2$) and aluminium hydroxide {$Al(OH)_3$ } results in the formation of cubes and more rarely dodecahedrons[26,27,31] and this is confirmed by the morphological features observed in Plates 1 and 2.

TABLE 8

X-RAY DIFFRACTION DATA FOR TRICALCIUM HYDROALUMINATE FORMATION AT A $Ca(OH)_2/Al(OH)_3$ MOLAR RATIO OF 1.5

(Cu Ka Radiation and Ni Filter)

2Ø (deg)	d-spacing (Å)	Rel. Int. (%)	Identified Phase
17.3	5.12	100	$3CaO.Al_2O_3.6H_2O$
20.0	4.41	55	$3CaO.Al_2O_3.6H_2O$
26.6	3.35	79	$3CaO.Al_2O_3.6H_2O$
28.4	3.31	65	$3CaO.Al_2O_3.6H_2O$
31.9	2.80	95	$3CaO.Al_2O_3.6H_2O$
35.0	2.55	26	$3CaO.Al_2O_3.6H_2O$
36.5	2.53	39	$3CaO.Al_2O_3.6H_2O$
39.3	2.29	100	$3CaO.Al_2O_3.6H_2O$
44.5	2.03	91	$3CaO.Al_2O_3.6H_2O$
45.7	1.98	18	$3CaO.Al_2O_3.6H_2O$
50.3	1.81	18	$3CaO.Al_2O_3.6H_2O$
52.5	1.74	38	$3CaO.Al_2O_3.6H_2O$
53.6	1.71	27	$3CaO.Al_2O_3.6H_2O$
54.6	1.68	49	$3CaO.Al_2O_3.6H_2O$
58.8	1.57	22	$3CaO.Al_2O_3.6H_2O$
62.7	1.48	13	$3CaO.Al_2O_3.6H_2O$
66.3	1.40	17	$3CaO.Al_2O_3.6H_2O$
68.6	1.37	13	$3CaO.Al_2O_3.6H_2O$
69.3	1.35	12	$3CaO.Al_2O_3.6H_2O$

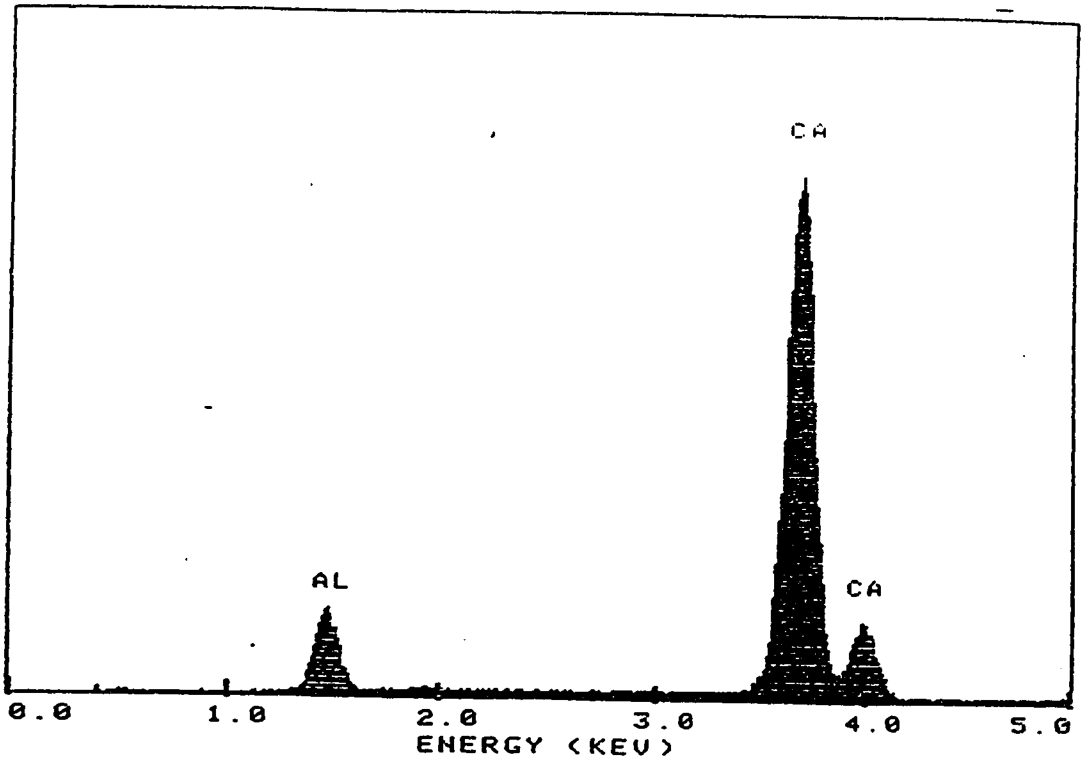


Figure 17. Energy Dispersive X-Ray Spectrum of Tricalcium Hydroaluminate Precursor

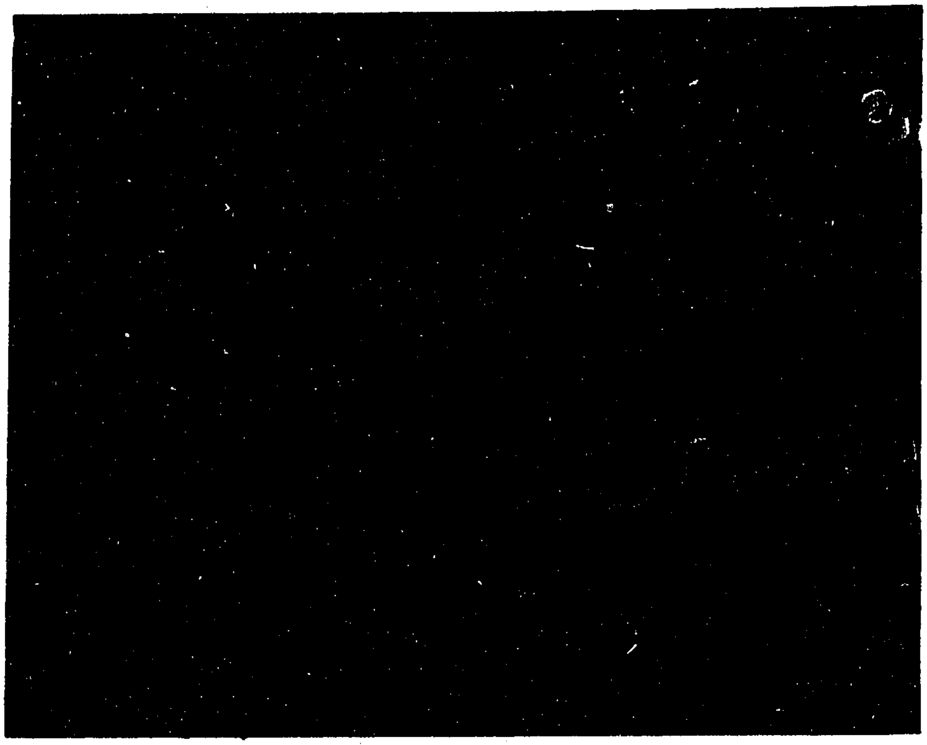


PLATE 1 SEM MICROGRAPH OF TRICALCIUM HYDROALUMINATE PRECURSOR (X 1500) RIGHT HAND MARKER = 20 μm

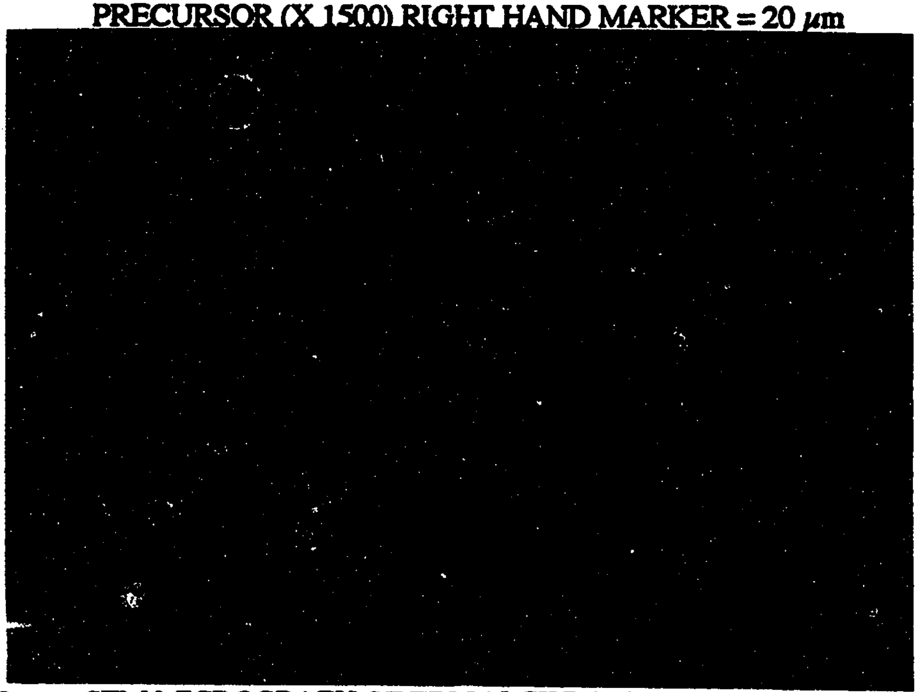


PLATE 2 SEM MICROGRAPH OF TRICALCIUM HYDROALUMINATE PRECURSOR (X 1500) RIGHT HAND MARKER = 10 μm

4.3 DESILICONIZATION STUDIES

In order to determine the ratio which gives the most active tricalcium hydroaluminate precursor during hydrothermal treatment, $Ca(OH)_2/ Al(OH)_3$ ratios of 0.5, 1.0, 1.5 and 2.0 were used. The tricalcium hydroaluminate precursor formed were tested for silica removal activities using the Shell and Esso produced water samples. Figure 18 present the effect of the $Ca(OH)_2/Al(OH)_2$ mole ratio used in the precursor preparation on the silica removal activities. The figure indicate that the $Ca(OH)_2/Al(OH)_2$ mole ratio of 1.5 gave the most active tricalcium hydroaluminate precursor in terms of silica removal. Consequently, the precursor used in all the desiliconization studies were prepared at this ratio.

Figure 19 presents the variation in silica concentration with time for desiliconization reactions at 23°C (296°K), for the Shell and Esso samples. The pH data are final values taken at the end of the reaction. The two samples show rapid decline in silica content within the first minute of reaction, followed by an apparent induction period between one and five minutes of reaction, and a final silica removal stage. The initial decline of silica in solution is attributable to the rapid adsorption of silica onto the surface of the tricalcium hydroaluminate. After this initial surface adsorption, the silica is subsequently incorporated into the hydroaluminate structure to form a hydrogarnet. This incorporation step is responsible for the induction period shown in Figure 19. After the induction period, the hydrogarnet formed exerts an autocatalytic effect on further silica fixation, leading to the additional removal of silica from solution. The silica content of the Esso sample decreased to a zero value after fifteen minutes of reaction, while that in the Shell sample stabilized at about 100 ppm at 23°C.

The lower silica removal from the Shell sample can be attributed to the presence of a higher concentration of carbonate and bicarbonate species in the sample. The presence of these carbonates lead to the dissolution of some of the tricalcium hydroaluminate precursor as shown earlier in equation 7. This partial dissolution results in a lower effectiveness for silica removal. However, this problem can be solved by increasing the relative amounts of the hydroaluminate precursor used for the desiliconization of samples containing high carbonate ions, at ambient temperatures. Alternatively, since the dissolution of hydroaluminate by carbonate ions is a relatively slow reaction, an increase in the reaction temperature above ambient, enhances the rate of incorporation of the initially adsorbed silica into the hydroaluminate matrix to form the hydrogarnet product, which is more resistant to dissolution by carbonate ions.

In this case, the induction period for silica incorporation is significant reduced, and the silica concentration in solution approaches zero before any the dissolution of the precursor occurs. This temperature effect is illustrated in Figure 20 and 21, where the desiliconization reaction was conducted at 55°C (328°C) and 85°C respectively. The results in Figure 20 show that at 55°C, and for similar amounts of hydroaluminate precursor, the silica concentration in the Shell samples falls bellow 10 ppm after 15 minutes of reaction. The rates of silica removal are increased in both samples, and the induction period observed in Figure 19 is virtually eliminated. Figure 21 illustrates the silica removal process at 85°C (358°K) for the Esso- and Shell-produced water samples. At this temperature, most of the silica removal occur within one minute of reaction. The concentration of silica in both samples is reduced to below 5 ppm much more rapidly than at lower temperatures. In addition, no induction period is observed at 85°C.

The pH of the solution increases from an average of about 7.0 for the feed to between 8.0 and 10.5 for the final solution after desiliconization. The increase in pH is due to a combination of factors, including the release of hydroxyl ions during the actual silica removal step in accordance with Equation 6 and the formation of $Ca(OH)_2$ from dissolved calcium ions.

Using the desiliconization data in Figure 20, the order of reaction was determined using the Vant Hoff differential method. Silica removal was found to be a pseudo first order reaction. Assuming that temperature variation does not change the mechanism of the desiliconization reaction, and that the system is governed by the Arrhenius law, the activation energy for the silica removal was found to be E_A = 8.8 K cal mol^{-1}(37KJ/mol). The Arrhenius plot is shown in Figure 22. The activation energy value E_A = 8.8 K cal/mol indicates that the reaction is limited by a physical phenomenon (diffusion) rather than a chemical reaction. The E_A value of 8.8 Kcal/mol falls within the range for a boundary layer diffusion controlled reaction. It appears that the diffusion of silicon or silicate ions from the bulk solution, through the solid-liquid boundary layer is rate limiting with this desiliconization process.

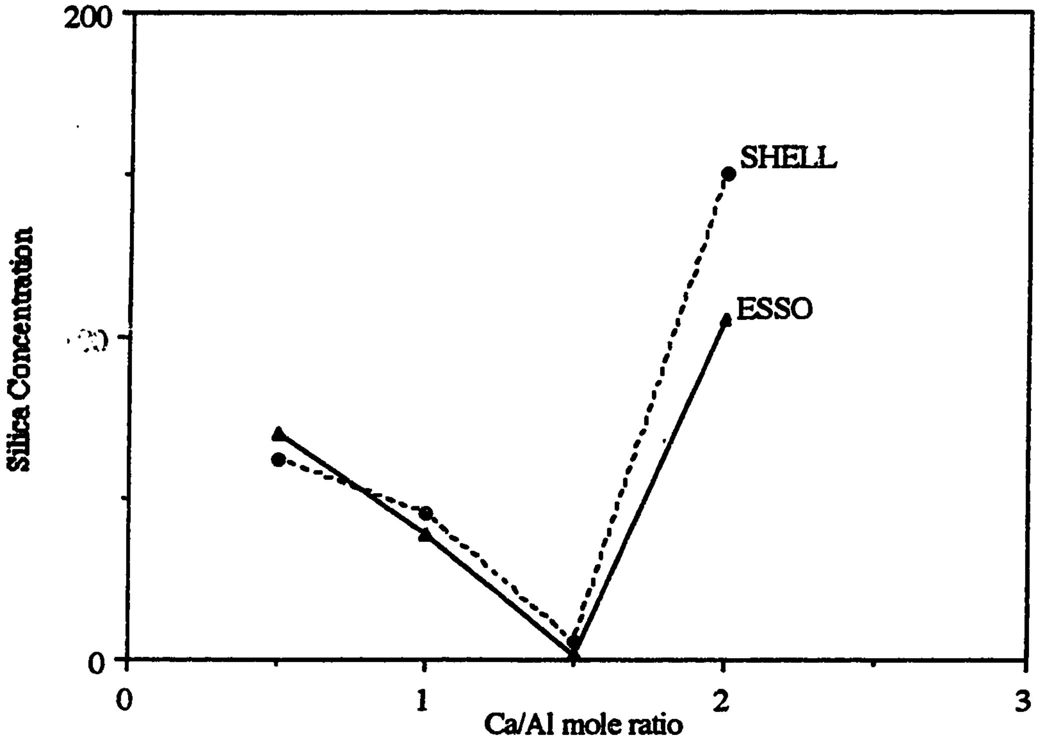


Figure 18. The Effect of $Ca(OH)_2/Al(OH)_3$ Mole Ratio for Precursor Preparation on Final Silica Concentration for Esso and Shell Water after Desiliconization at 85°C and 30 min Reaction Time (Tricalcium Hydroaluminate Preparation Conditions; 150°C, 100 psi, 1hr: Water to Precursor Ratio = 231:1)

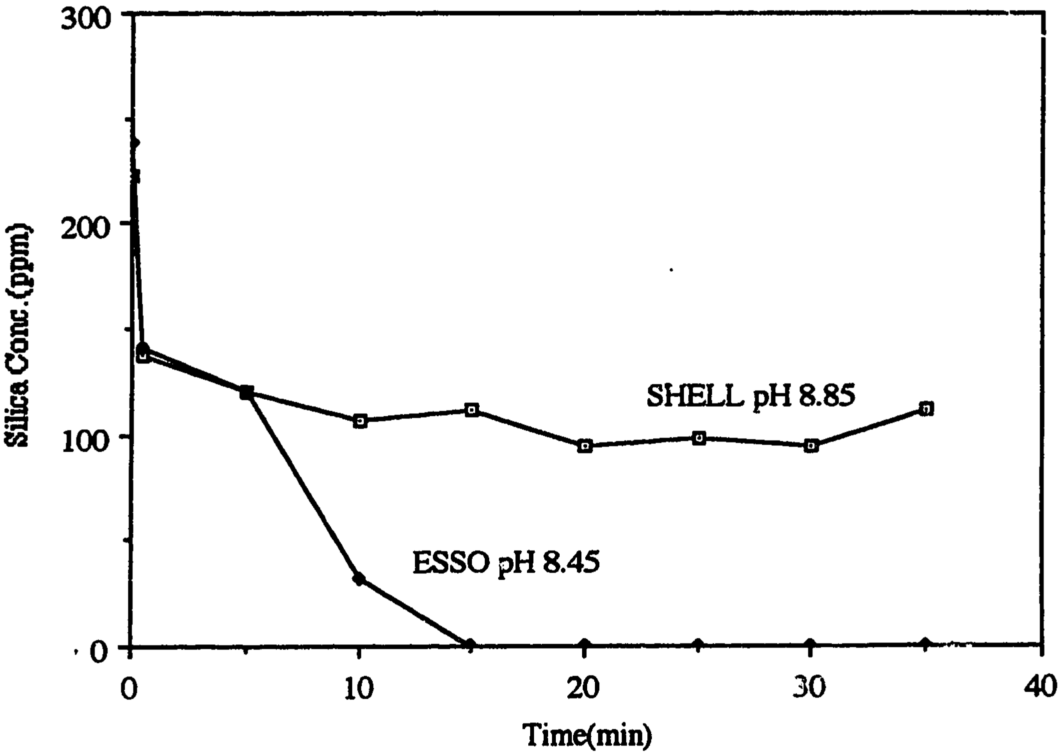


Figure 19. Variation in Dissolved Silica Concentration with Time for Shell and Esso Water During Desiliconization at 23°C (Water to Precursor Ratio = 231:1)

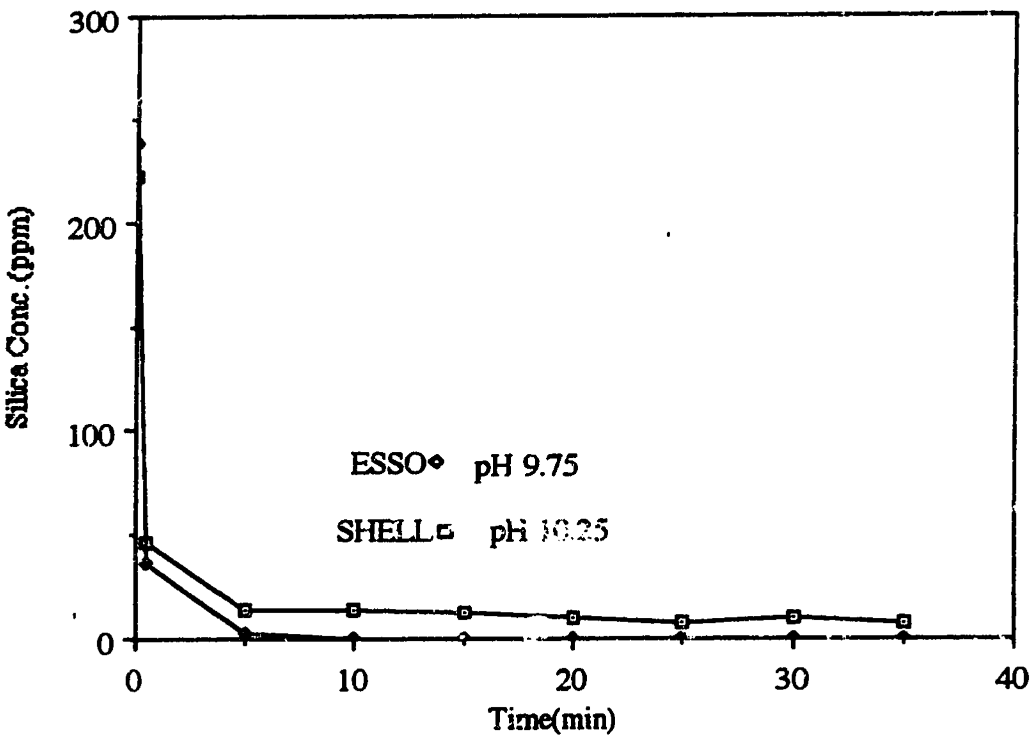


Figure 20. Variation in Dissolved Silica Concentration with Time for Shell and Esso Water During Desiliconization at 55°C (Water to Precursor Ratio = 231:1)

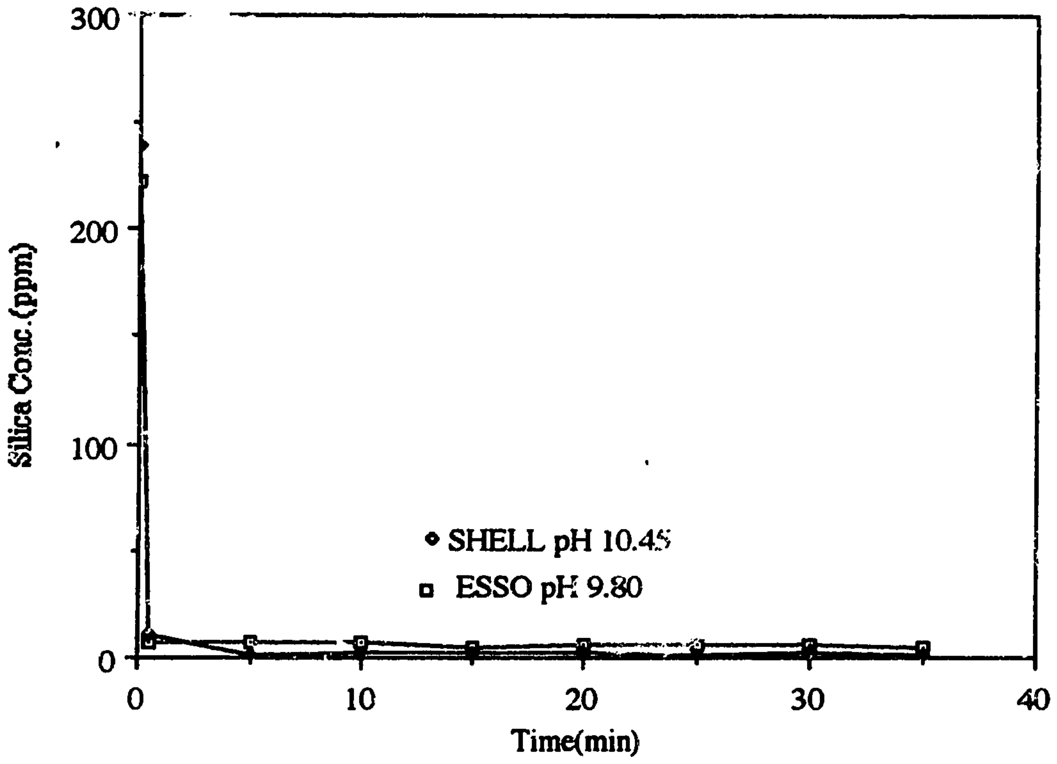


Figure 21. Variation in Dissolved Silica Concentration with Time for Shell and Esso Water During Desiliconization at 85°C , Water to Solid Ratio = 231:1)

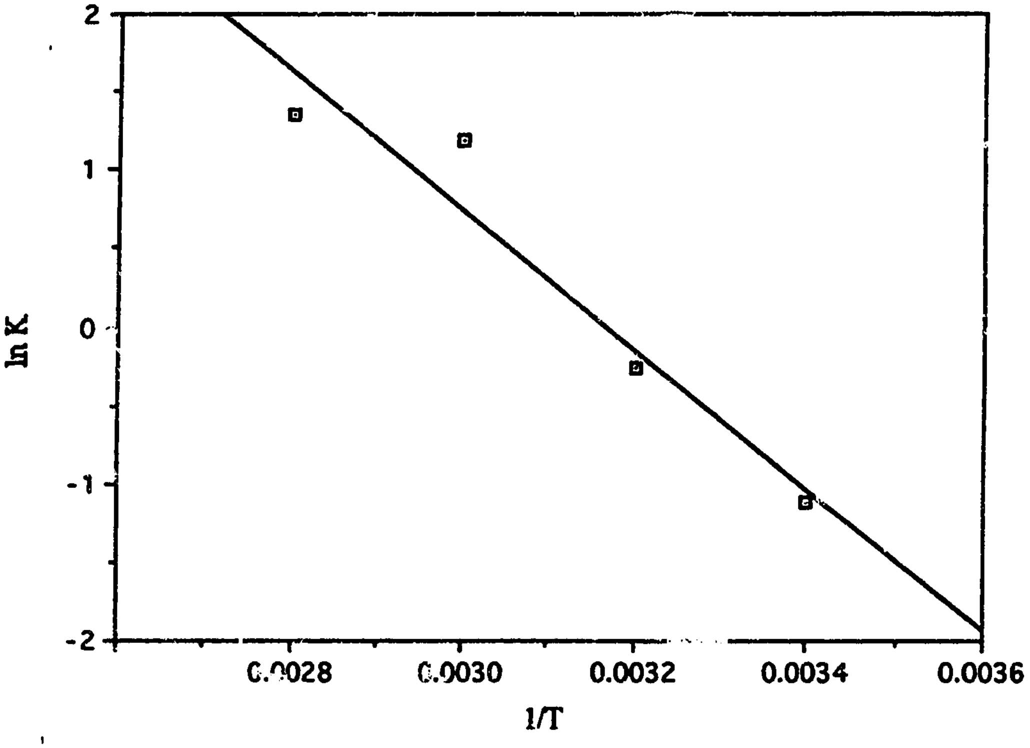


Figure 22. Arrhenius Plot for the Desiliconization Reaction.

Figures 23, 24 and 25 present the changes in magnesium concentration with time for the two samples, at 23°C, 55°C and 85°C respectively. The figures show significant reductions in the content of dissolved magnesium in the two samples during desiliconization. The magnesium reduction is presumably due to the precipitation of $Mg(OH)_2$ on the surface of the hydrogarnet. The increase in pH during the desiliconization reaction favour the precipitation of magnesium Higher magnesium removal is generally indicated with increasing reaction temperature in agreement with higher pH values with temperature. The variation in the content of dissolved calcium with time during desiliconization at 23°C, 55°C and 85°C are shown in Figures 26, 27 and 28 respectively. At 23°C, the dissolved calcium content increases significantly for both samples. The calcium content in the Esso sample increases from 72 ppm to about 140 ppm while it increases from 33 ppm to 95 ppm for the Shell sample

The increase in the dissolved calcium are attributable to the dissolution of some of the tricalcium hydroaluminate in the presence of carbonate ions. However, at elevated temperatures (55°C and 85°C), correspondingly higher dissolved calcium is observed for the Esso sample, while the Shell sample showed little or no additional calcium dissolution beyond the feed level. This observation can be explained by the fact that with the Shell sample, the dissolved calcium is rapidly reprecipitated as $CaCO_3$ as a result of the high carbonate content of the Shell-produced water. This reprecipitation reaction, being a relatively slow one, is enhanced at elevated temperatures, hence no net increase in dissolved calcium are observed in the shell sample at 55°C and 85°C. This reprecipitation reaction also occurs in the Esso sample to a lesser degree because of the lower carbonate concentration. Given enough time, the reprecipitation of dissolved calcium as $CaCO_3$ will also occur at 23°C.

This is clearly indicated in Figure 26 where it is seen that beyond 30 minutes of reaction time, the calcium concentration starts to decline in both the Esso and Shell samples. However, the additional dissolution of calcium during the desiliconization reaction will not constitute a problem in produced water treatment, since calcium and other multivalent elements in solution (except silicon) are readily removed in a final polishing step with ion exchange resins. The dissolution of some tricalcium hydroaluminate in the presence of carbonate ions will also be expected to increase the amount of dissolved aluminium ions during desiliconization. This expectation is confirmed in the data presented in Figures 29 and 30. The dissolved alumina content is found to increase during the desiliconization reaction. Higher dissolved alumina content is observed for the Shell sample due to the higher carbonate content in this sample. However, as with dissolved calcium ions, aluminium ions in solution are readily removed during the polishing step with ion exchange resins for TDS removal. Thus, an increase in dissolved alumina will not pose the kind of problems associated with dissolved silica.

A simple pH adjustment of the desiliconized solution from a pH of a about 10 to 6 will readily precipitate dissolved aluminium ions as the hydroxide, which could be removed before subsequent polishing. Such a pH adjustment carried out during this study showed that aluminium concentration was reduced from about 175 ppm to less than 2 ppm. The X-ray diffraction data obtained for the solid residue from desiliconization are shown in Tables 9 and 10 for Esso and Shell water respectively. These residues were obtained from the 85°C desiliconization reactions by filtration.

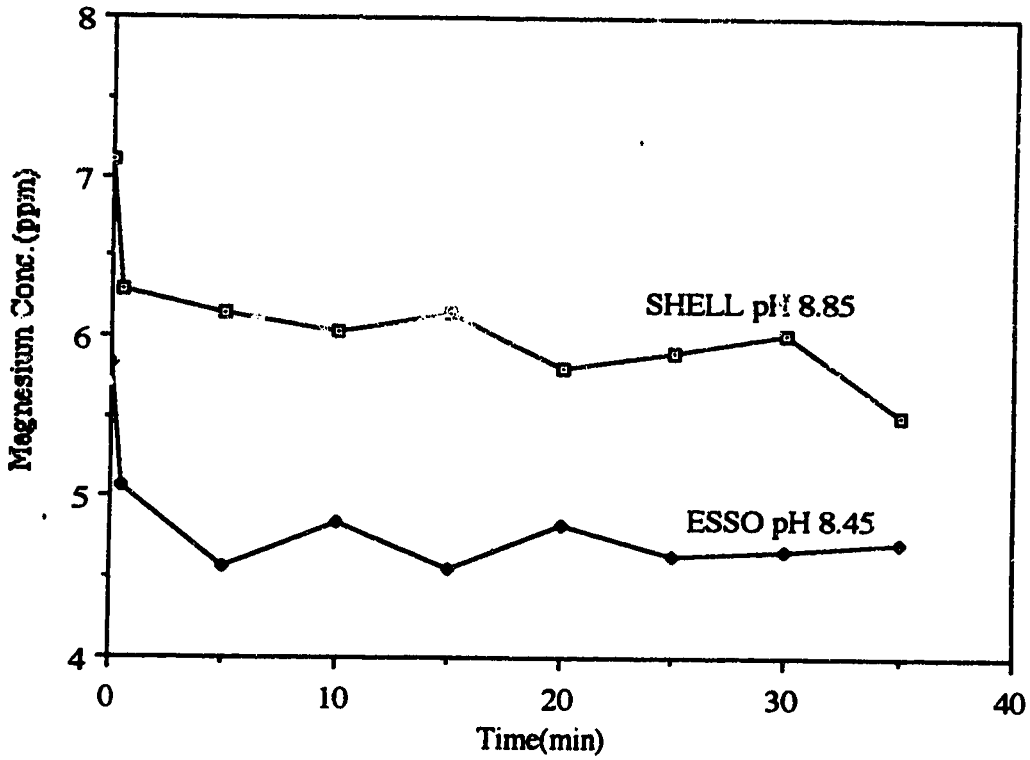


Figure 23. Changes in Dissolved Magnesium Concentration with Time for Shell and Esso Water During Desiliconization at 23°C (Water to Solid Ratio = 231:1)

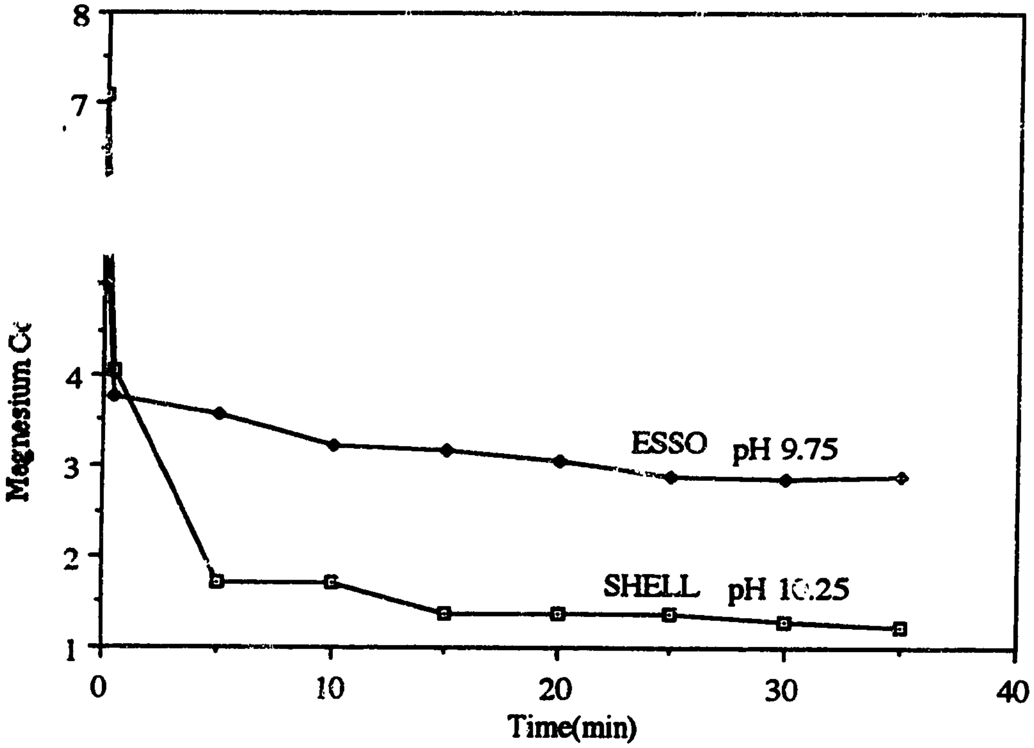


Figure 24. Changes in Dissolved Magnesium Concentration with Time for Shell and Esso Water During Desiliconization at 55°C (Water to Solid Ratio = 231:1)

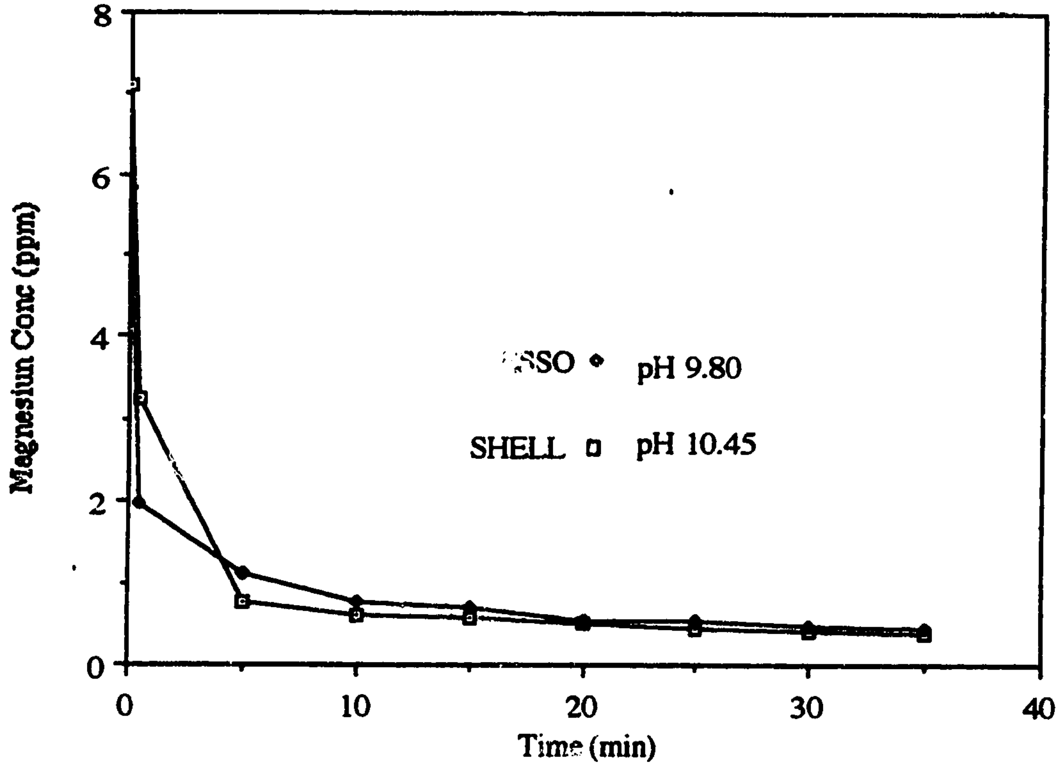


Figure 25. Changes in Dissolved Magnesium Concentration with Time for Shell and Esso Water During Desiliconization at 85°C (Water to Solid Ratio = 231:1)

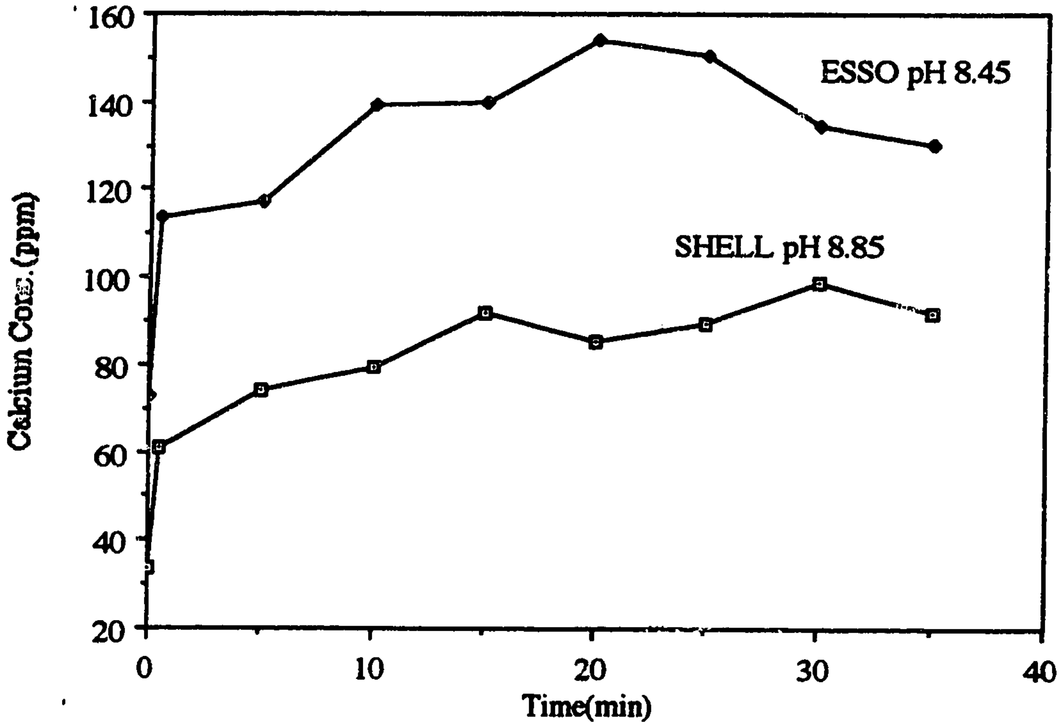


Figure 26. Variation in Dissolved Calcium Concentration with Time for Shell and Esso Water During Desiliconization at 23°C (Water to Solid Ratio = 231:1)

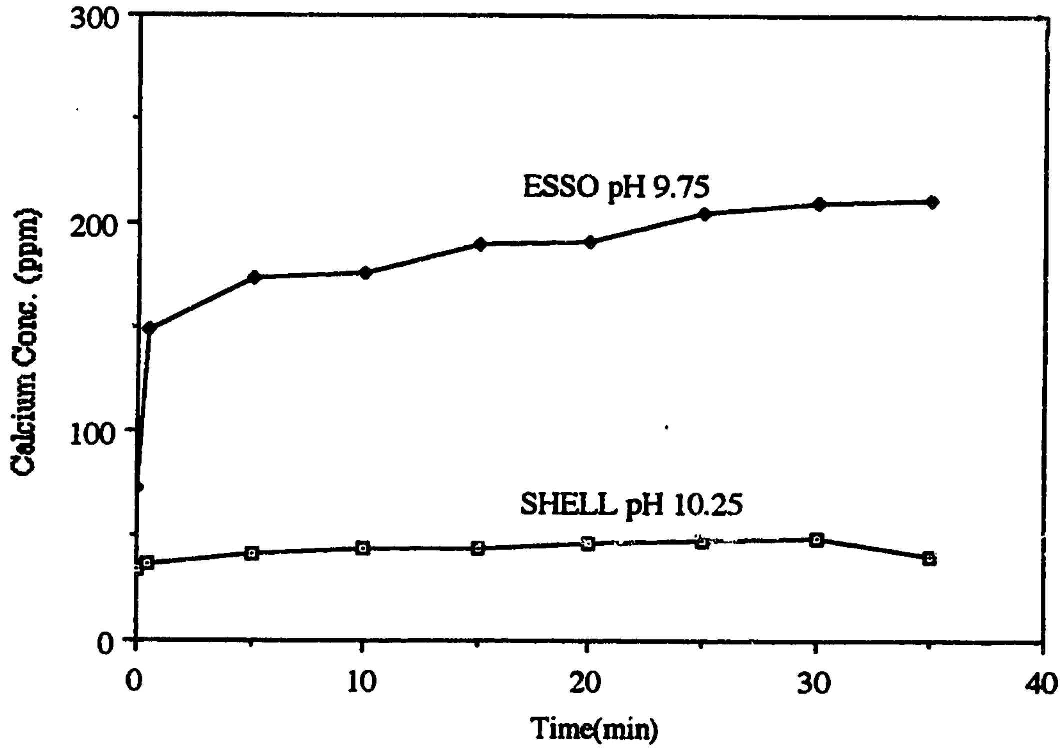


Figure 27. Variation in Dissolved Calcium Concentration with Time for Shell and Esso Water During Desiliconization at 55°C (Water to Solid Ratio = 231:1)

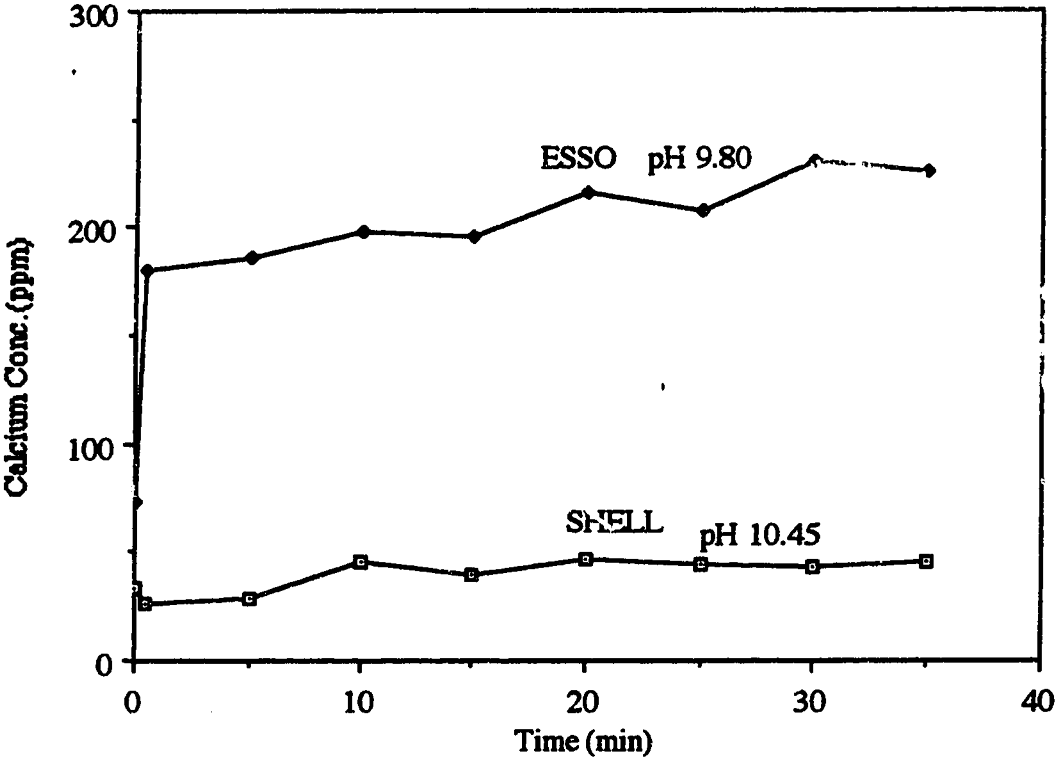


Figure 28. Variation in Dissolved Calcium Concentration with Time for Shell and Esso Water During Desiliconization at 85°C (Water to Solid Ratio = 231:1)

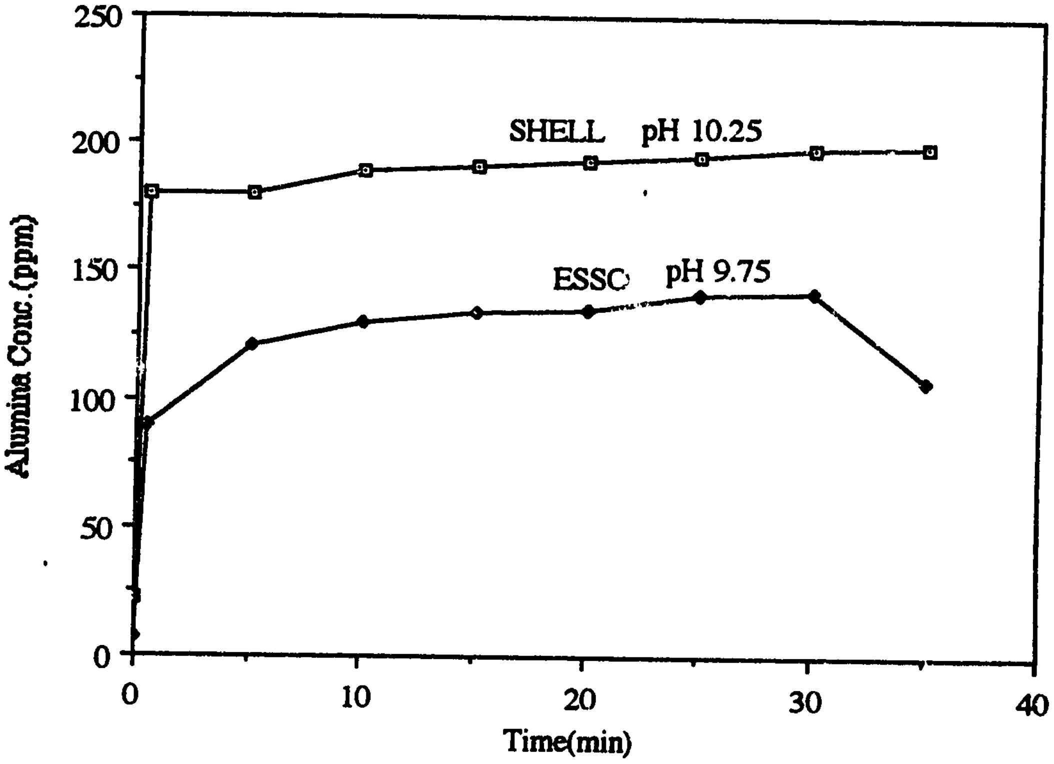


Figure 29. Plot of Dissolved Alumina Concentration with Time for Esso and Shell Water During Desiliconization at 55°C (Water to Solid Ratio = 231:1)

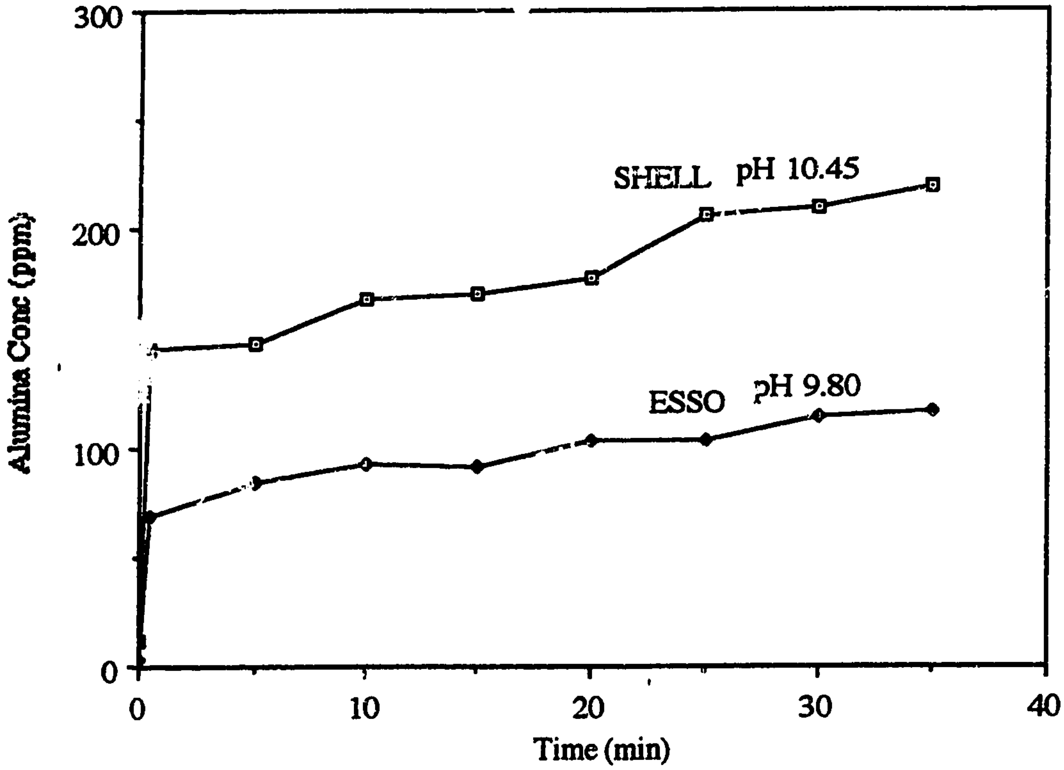


Figure 30. Plot of Dissolved Alumina Concentration with Time for Esso and Shell Water During Desiliconization at 85°C(Water to Solid Ratio = 231:1)

In addition, the data for Esso residue (Table 9) show the presence of precipitated NaCl which was not observed in the Shell residue. This is expected, since the Esso-produced water contains much higher content of dissolved sodium than the Shell sample (Table 4). The corresponding SEM/EDS spectra for the Esso and Shell desiliconization solid residue are shown in Figures 31 and 32 respectively. These spectra also confirm the presence of silicon in the residues. Furthermore, a Cl^- ion peak is observed in the Esso spectrum but not in the shell spectrum in agreement with the x-ray diffraction results.

Plates 3 and 4 show SEM micrograph of the desiliconization precipitate. It is observed that there is a high degree of agglomeration of the particles from the morphological features revealed at the surface of the precipitate to a depth of 5×10^{-3} μm. Thus, no separate particles of SiO_2, $Ca(OH)_2$ and $Al(OH)_3$ can be seen; instead a well-developed interparticle cementation surface is clearly evident. This results were found to be in agreement with X-ray diffraction measurements (Tables 9 and 10). This agglomeration makes the subsequent filteration of the desiliconization residue relatively easy to accomplish.

TABLE 9

X-RAY DIFFRACTION FOR DESILICONIZATION PROCESS RESIDUE FROM ESSO-PRODUCED WATER (Cu Ka Radiation and Nickel Filter)

20 (deg)	d-spacing (Å)	Rel. Int (%)	Identified Phase
18.61	4.74	44	$Mg(OH)_2$
38.2	2.36	41	$Mg(OH)_2$
51.0	1.79	17	$Mg(OH)_2$
58.9	1.57	15	$Mg(OH)_2$
10.9	8.11	100	$3CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$
21.8	4.07	41	$3CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$
33.0	10.50	15	$3CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$
29.50	3.03	39	$CaCO_3$
38.00	2.27	17	$CaCO_3$
47.70	1.91	12	$CaCO_3$
48.90	1.87	11	$CaCO_3$
31.80	2.81	25	NaCl
57.60	11.62	10	NaCl

TABLE 10

X-RAY DIFFRACTION FOR DESILICONIZATION PROCESS RESIDUE FROM SHELL-PRODUCED WATER (Cu Ka Radiation and Nickel Filter)

2Ø (deg)	d-spacing (Å)	Rel. Int (%)	Identified Phase
18.7	4.14	10	$Mg(OH)_2$
33.0	2.71	25	$Mg(OH)_2$
38.2	2.35	100	$Mg(OH)_2$
51.0	1.79	53	$Mg(OH)_2$
58.9	1.57	39	$Mg(OH)_2$
62.4	1.49	21	$Mg(OH)_2$
68.4	1.37	19	$Mg(OH)_2$
72.2	1.27	19	$Mg(OH)_2$
29.4	3.03	25	$CaCO_3$
11.5	7.69	36	$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
22.8	3.90	28	$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

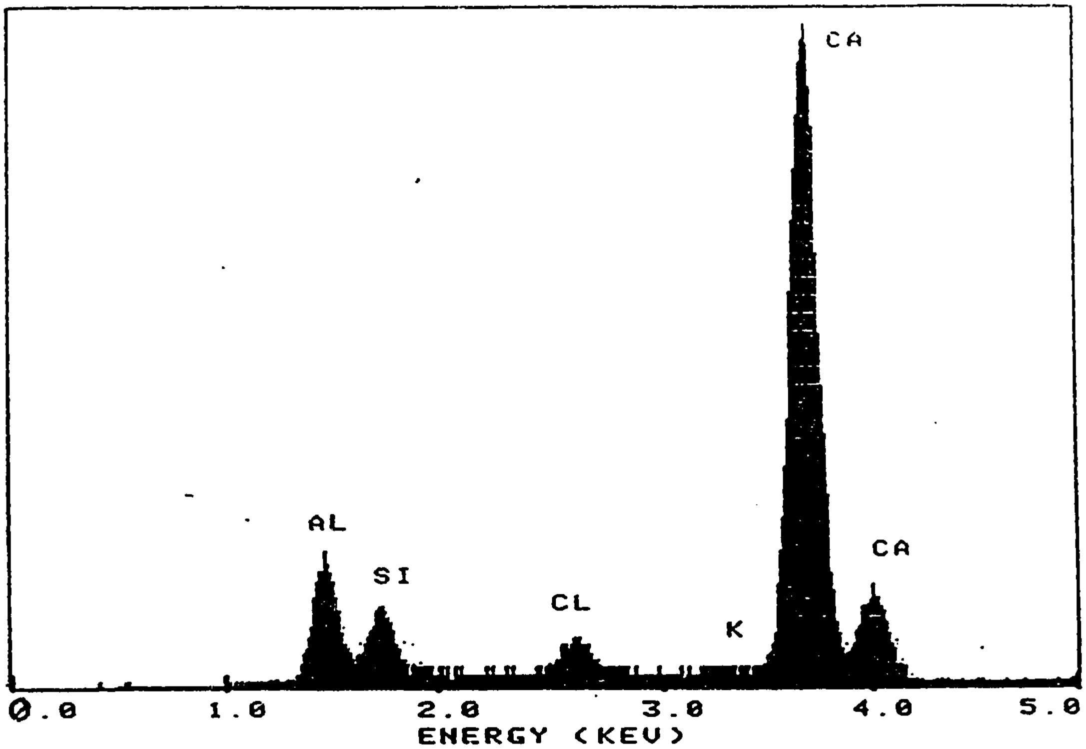


Figure 31. Energy Dispersive X-Ray Spectrum (EDS) of Desiliconization Solid Residue for Esso Water Sample (Desiliconization at 85°C)

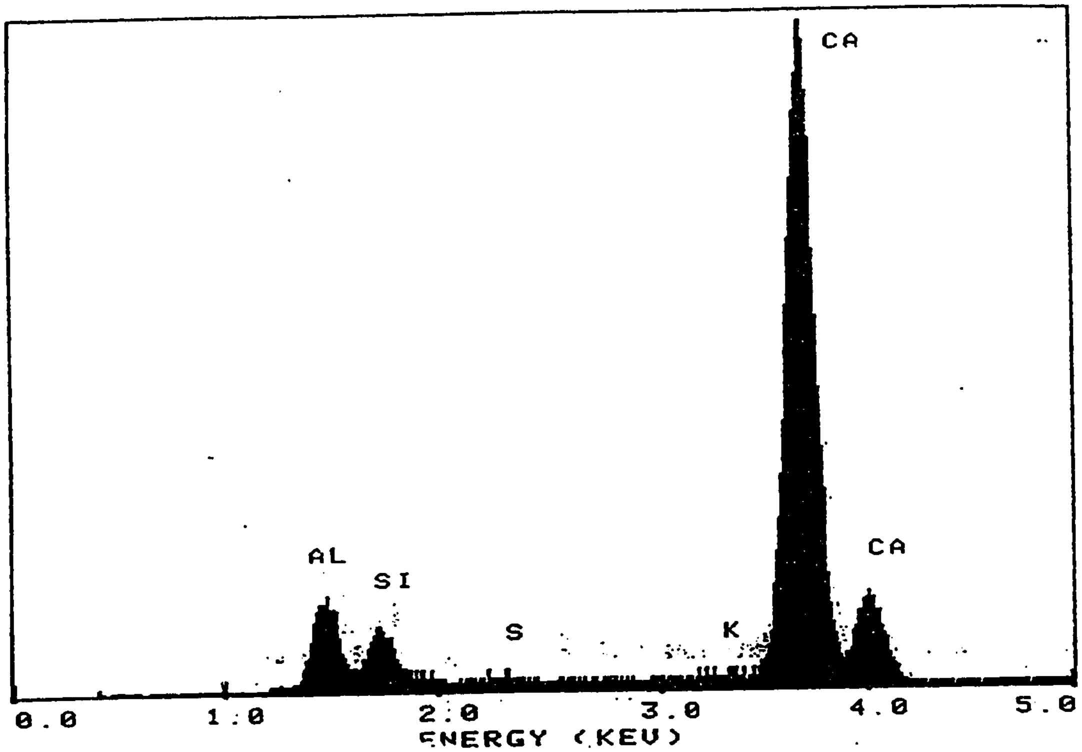


Figure 32. Energy Dispersive X-Ray Spectrum (EDS) of Desiliconization Solid Residue for Shell Water Sample (Desiliconization at 85°C)

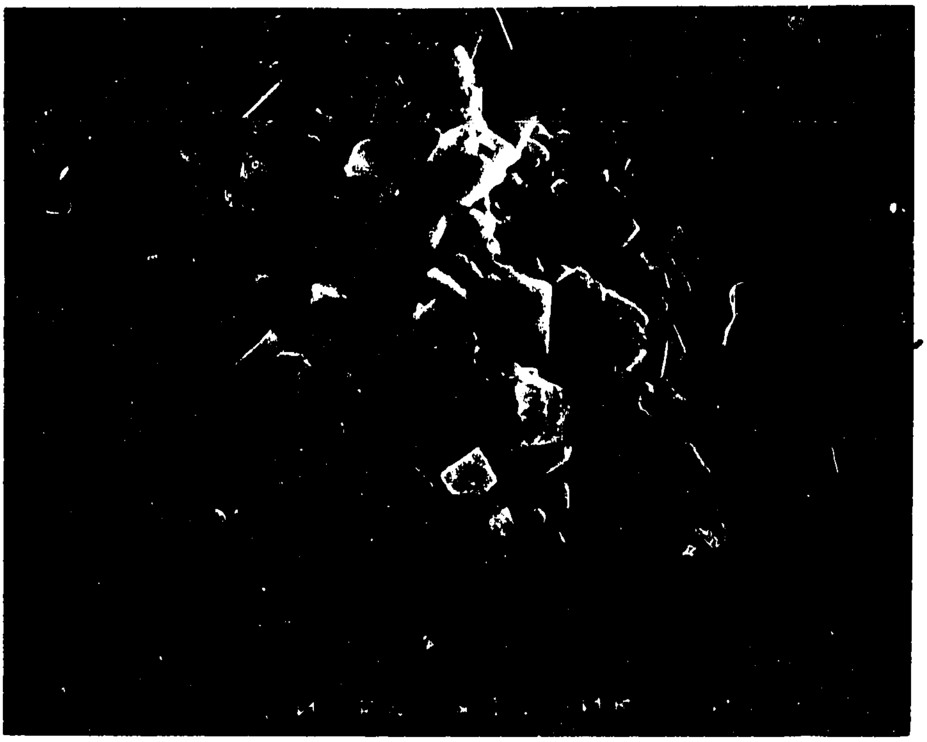


PLATE 3 SEM MICROGRAPH OF DESILICONIZATION PRECIPITATE

(X 1500) RIGHT HAND MARKER = 20 μm

PLATE 4 SEM MICROGRAPH OF DESILICONIZATION PRECIPITATE

(X 3000) RIGHT HAND MARKER = 10 μm

The diffraction data for both residues indicate the presence of $Mg(OH)_2$,$CaCO_3$ and the hydrogarnet product ($3CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$). These results confirm the formation of hydrogarnet during silica removal from produced water. A determination of the residual total dissolved solids (TDS) content of the 85°C desiliconized water samples showed that the TDS contents decreased by about 800 mg/l for both samples. TDS for the Esso sample decreased from 8500 mg/l to 7650 mg/l while that for Shell decreased from 3000 mg/l to 2200 mg/l. This shows that in addition to silica removal, some TDS compounds are removed from the produced water during desiliconization by the hydrogarnet process. At these TDS levels, and with the dissolved silica removed, only a limited additional polishing step will be required before recycling through steam generators.

4.3.1 EFFECT OF WATER TO PRECURSOR RATIO ON DESILICONIZATION

Figure 33 illustrates the effect of water to precursor ratio on final silica concentration during the desiliconization of shell produced water using untreated, decarbonated water-1 and decarbonated water-2 samples. It is observed from this figure that, at a water to precursor ratio of 300, the silica content of all the waters decreased to nearly zero, but at a water to precursor ratio of 600 to 900, the silica content of the untreated water increased from 50 ppm to 170 ppm whilst the silica content of the pretreated waters increased slightly but remained below 50 ppm. This data indicate that, the removal of the carbonates and bicarbonates is an important prerequisite to the effective removal of the silica and silicates from solution by tricalcium hydroaluminate. The pH of all the samples at water to precursor ratio of 300, 600 and 900 were similar and ranged between pH 9-11.

Figure 34 shows the effect of water to precursor ratio on final magnesium concentration during the desiliconization of shell produced water using untreated, decarbonated water-1 and decarbonated water-2 samples. It is observed that the magnesium ion content decreased from about 1.5 ppm to below 1 ppm with water to precursor ratio of 300 to 600 for both the untreated and pretreated waters. The marginal reduction of magnesium ion content in the untreated water as compared to the pretreated waters at water to precursor ratio of 900 support the suggestion that the precipitating calcium carbonate also helps in the magnesium removal as it acts as a precipitating surface[37].

Figure 35 presents the effect of water to precursor ratio on final calcium concentration in desiliconized shell produced waters using untreated and pretreated (Decarbonated-1 and 2) waters. The fact that the untreated water had the lowest silica content between 8 to 30 ppm at all the water to precursor ratios as compared to the pretreated waters, supports the suggestion that the dissolved calcium reprecipitated according to equation 7. The calcium ion content of the desiliconized pretreated (decarbonated-1 and 2) waters show similar trend. Although the carbonates and bicarbonate were to removed, a slight increase in calcium content in both waters suggest some dissolution of the precursor

Figure 36 presents the effect of water to solid ratio on final alumina concentration in desiliconized Shell produced water using untreated and pretreated (decarbonated 1 and 2) waters. The figure shows that, the dissolved alumina content of the untreated water was consistently higher than that in the decarbonated water samples at all water to precursor ratios studied This confirms that the dissolution of tricalcium hydroaluminate precursor by carbonates and bicarbonates releases aluminum ions into solution. Unlike calcium ion which could be reprecipitated as calcium carbonates due to the presence of excess

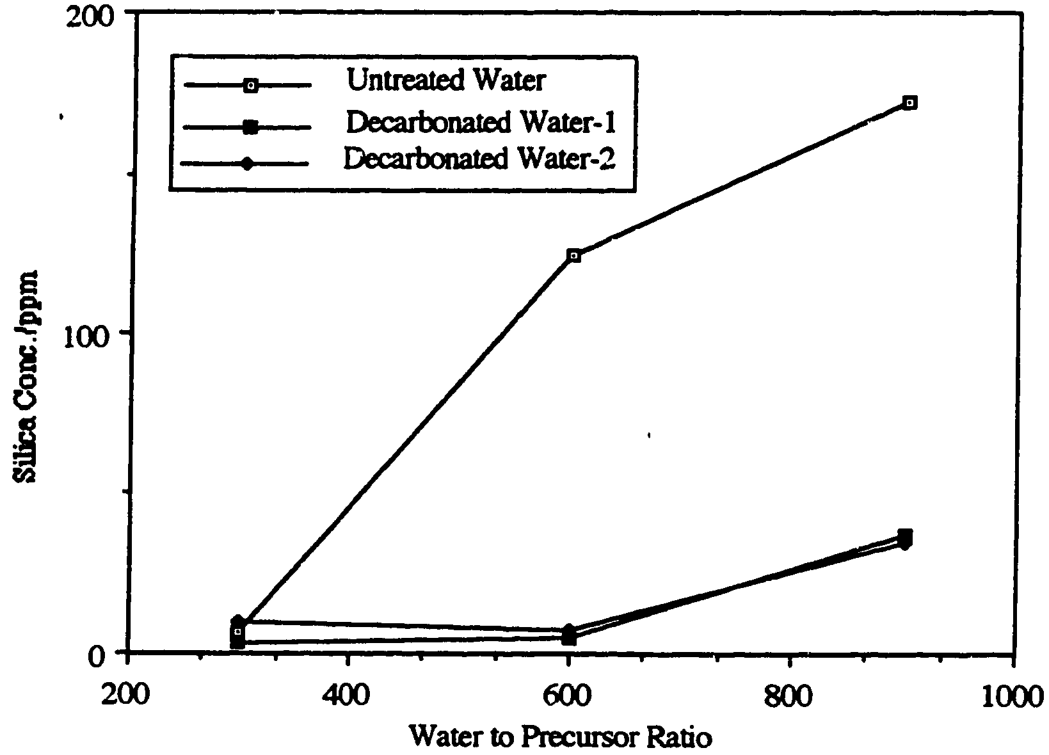


Figure 33. The Effect of Water to Precursor Ratio on Final Silica Concentration in Desiliconized Shell Produced Waters using Untreated and Pretreated (Decarbonated-1 and 2) Water(Reaction Conditions: Temperature 85°C, Time 30 min, Precursor $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$)

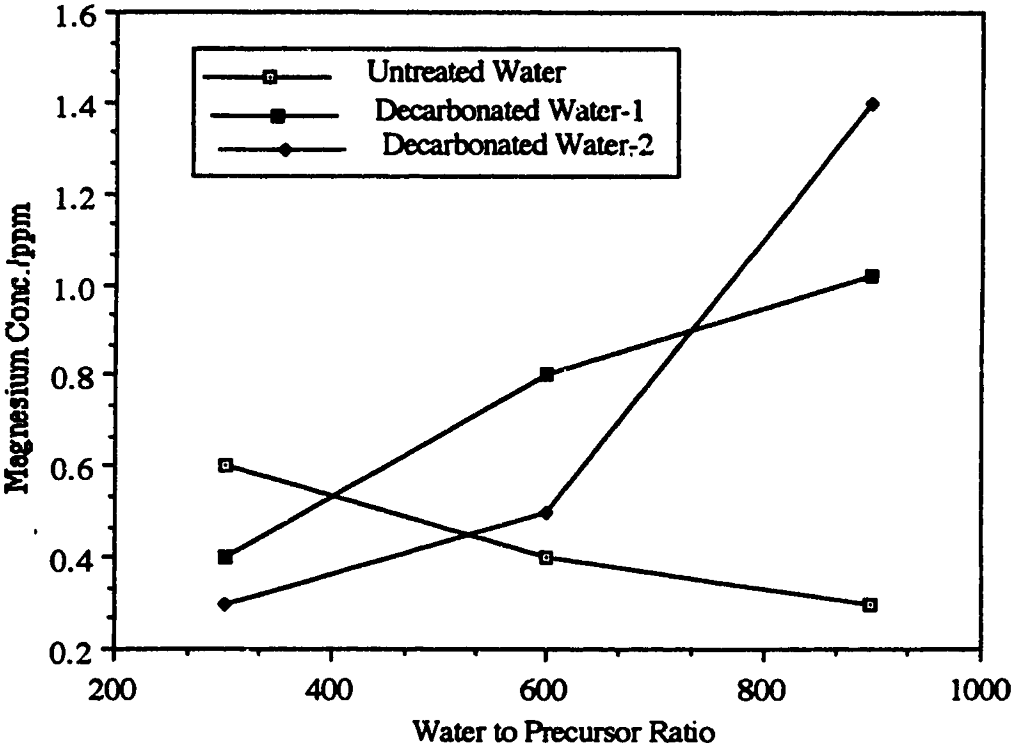


Figure 34. The Effect of Water to Precursor Ratio on Final Magnesium Concentration in Desiliconized Shell Produced Waters using Untreated and Pretreate (Decarbonated-1.and 2) Water (Reaction Conditions: Temperature 85°C, Time 30 min, Precursor $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$)

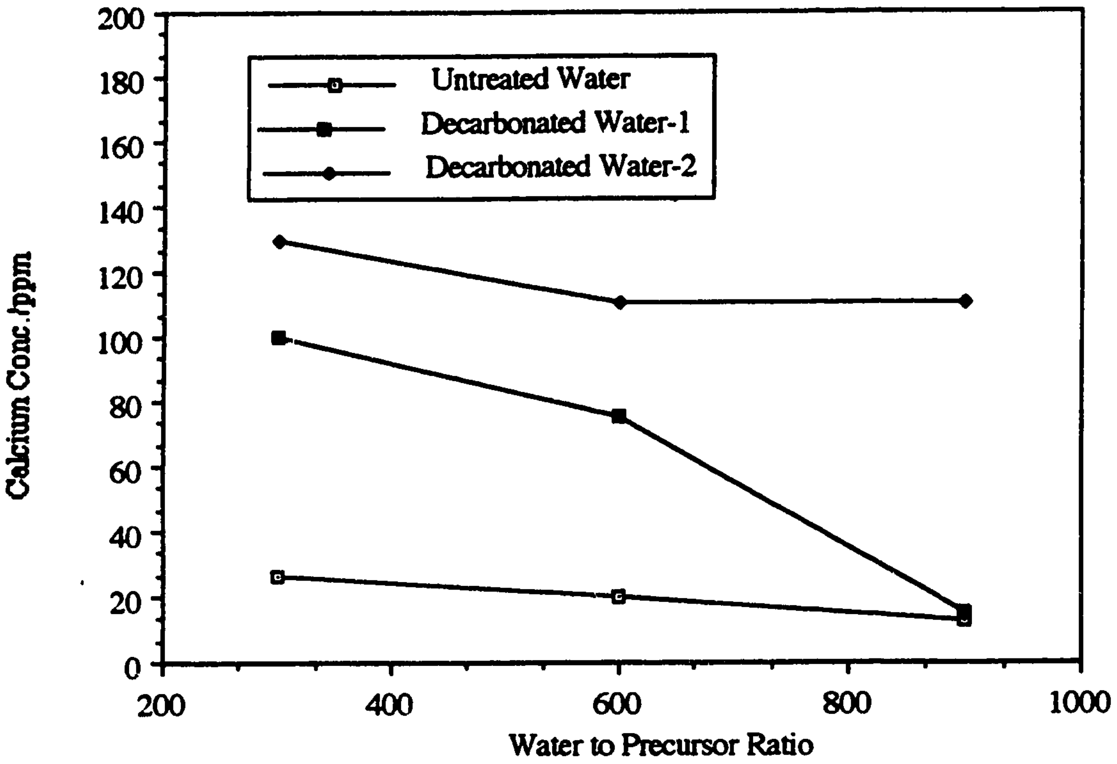


Figure 35. The Effect of Water to Precursor Ratio on Final Calcium Concentration in Desiliconized Shell Produced Waters using Untreated and Pretreated (Decarbonated - 1 and 2) Water (Reaction Conditions: Temperature 85°C, Time 30 min, Precursor $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$)

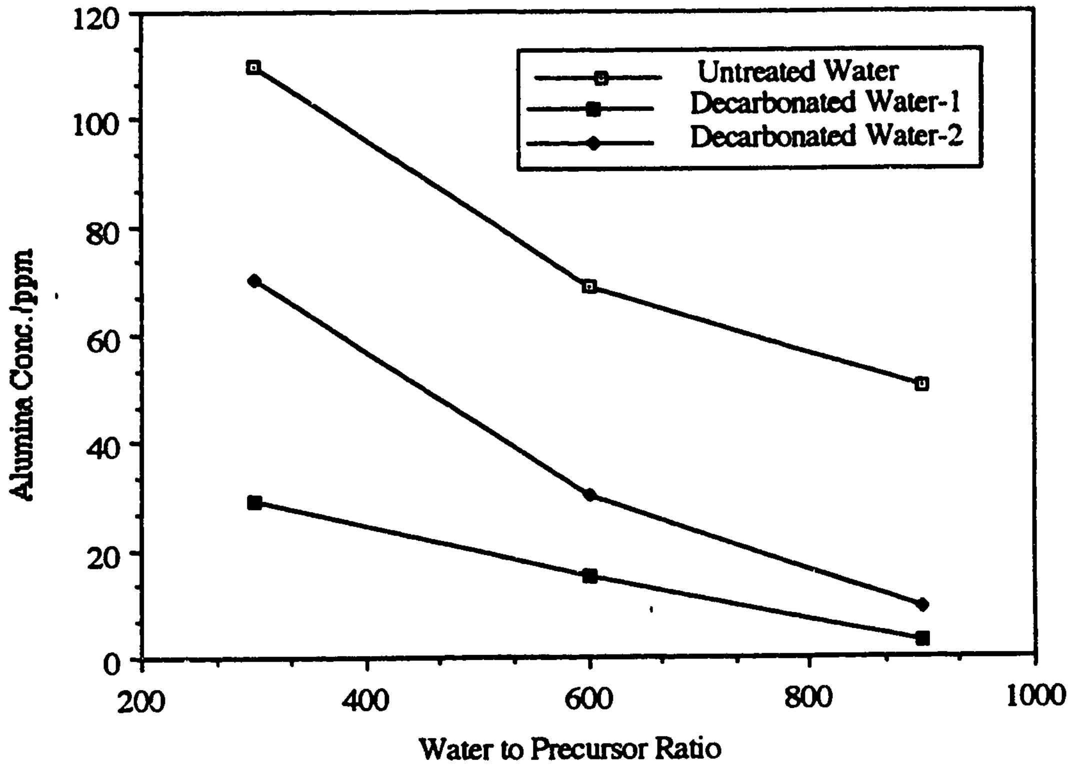


Figure 36. The Effect of Water to Precursor Ratio on Final Alumina Concentration in Desiliconized Shell Produced Waters using Untreated and Pretreated (Decarbonated-1and 2) Water(Reaction Conditions: Temperature 85°C,

carbonates in the untreated water, the aluminum ions remain in solution due to the prevailing pH of 10 as aluminum ions precipitates around pH of 6. The alumina content of the desiliconized pretreated (decarbonated 1 and 2) waters were slightly higher at water to precursor ratio of 300 but far less than that of the untreated water. The alumina content decreased from 70 ppm to 3 ppm at water to solid ratio of 900.as the dissolution of the tricalcium hydroaluminate was minimized by the elimination of the carbonates and bicarbonates. Figure 37 shows the effect of water to precursor ratio on final silica concentration using both ambient and autoclave prepared $3CaO\cdot Al_2O_3\cdot 6H_2O$ precursor. The ambient prepared was prepared at 23°C and atmospheric pressure. The figure also shows that, the autoclave prepared precursor is more effective in the removal of silica from the produced water, as the final silica concentration from the desiliconized water using autoclave prepared precursor is significant lower than that from the ambient prepared precursor. Figure 38 shows the effect of water to precursor ratio on final calcium concentration using both ambient and autoclave prepared precursor. From the figure it can be seen that, at water to precursor ratio of 300 , a high final calcium content of about 200 ppm is obtained from the desiliconized water from the ambient prepared precursor as compared to the autoclave prepared water of about 50ppm calcium.

This suggest that the tricalcium hydroaluminate precursor prepared at ambient conditions less stable as compared to the precursor.prepared in the autoclave. The calcium ion concentration decreased with increasing water to solid ratio for both precursors as expected. Figure 39 presents the effect of water to precursor ratio on final alumina concentration using both ambient and autoclave prepared precursor. The results from this figure show that the final alumina content of the desiliconized water from the ambient prepared precursor is less than that of the autoclave prepared precursor at all water to precursor ratios. The reason for this variation. needs to be investigated as the reverse should have been the case. Figure 40 illustrates the effect of water to precursor ratio on final magnesium concentration in desiliconized water using both ambient and autoclave prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor. At water to precursor ratio of 300 and 600 the magnesium ion content of desiliconized water from ambient prepared precursor is slightly lower than that of autoclave prepared precursor. But at a water to solid ratio of 900 the magnesium ion content of the desiliconized water from the autoclave prepared

precursor is far lower than that from the ambient prepared precursor. These results clearly demonstrate that in general, the autoclave prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor is more effective in the removal of silica from briny produced water. The total dissolved solids (TDS) of the desiliconized water from the autoclave prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor decreased from 3000 mg/l to 2150 mg/l on the average,whilst the TDS of the desiliconized water from the ambient prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor decreased from 3000 mg/l to 2600 mg/l.

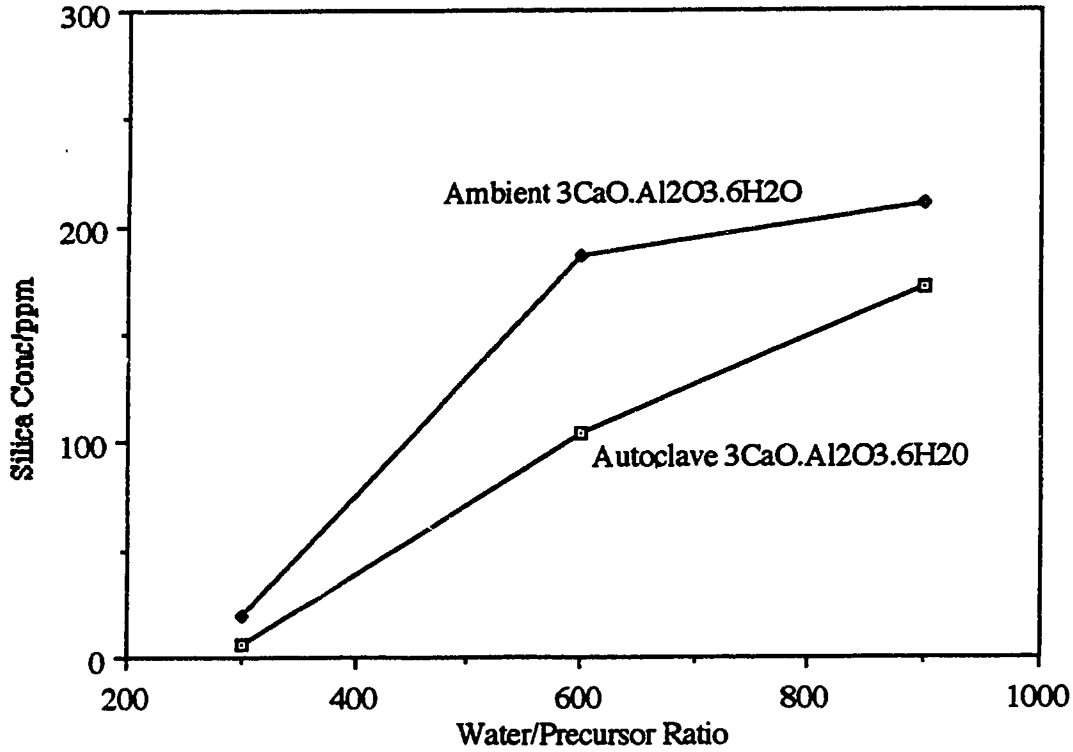


Figure 37. The Effect of Water to Precursor Ratio on Final Silica Concentration in Desiliconized Shell Produced Water using Autoclave and Ambient Prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor (Reaction Conditions: 85°C; 30 min;)

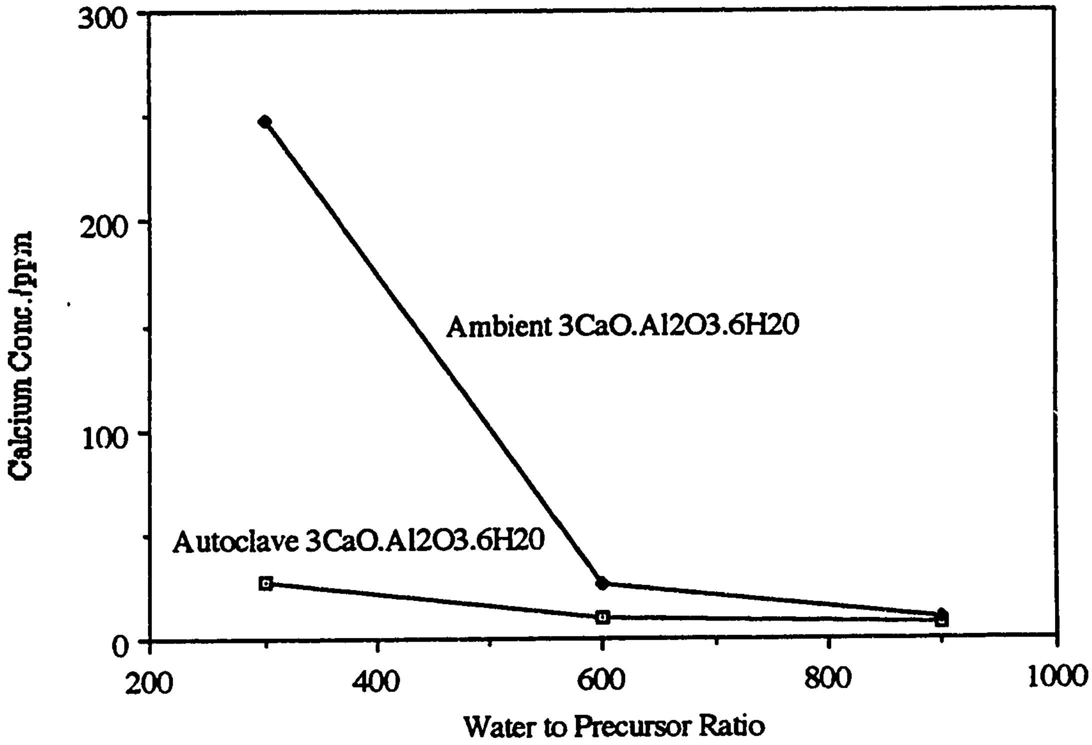


Figure 38. The Effect of Water to Precursor Ratio on Final Calcium Concentration in Desiliconized Shell Produced Water using Autoclave and Ambient Prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor (Reaction Conditions: 85°C; 30 min)

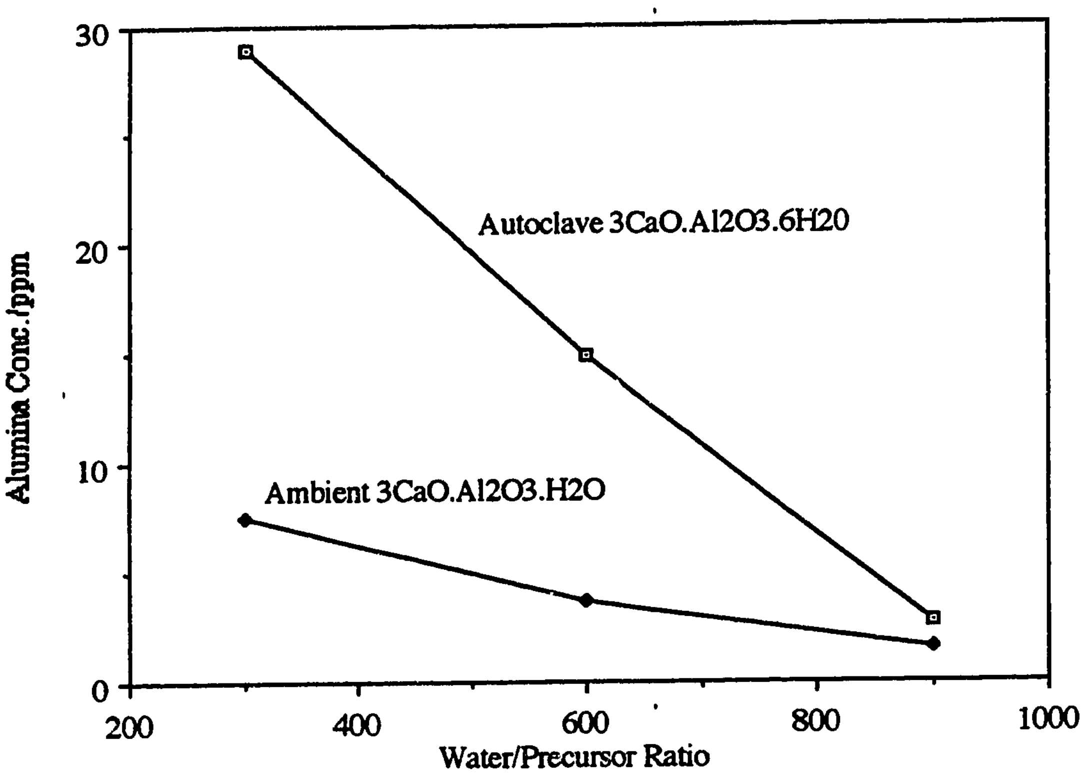


Figure 39. The effect of water to Precursor Ratio on Final Alumina Concentration in Desiliconized Shell Produced Water using Autoclave and Ambient Prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor (Reaction Conditions: 85°C; 30 min;)

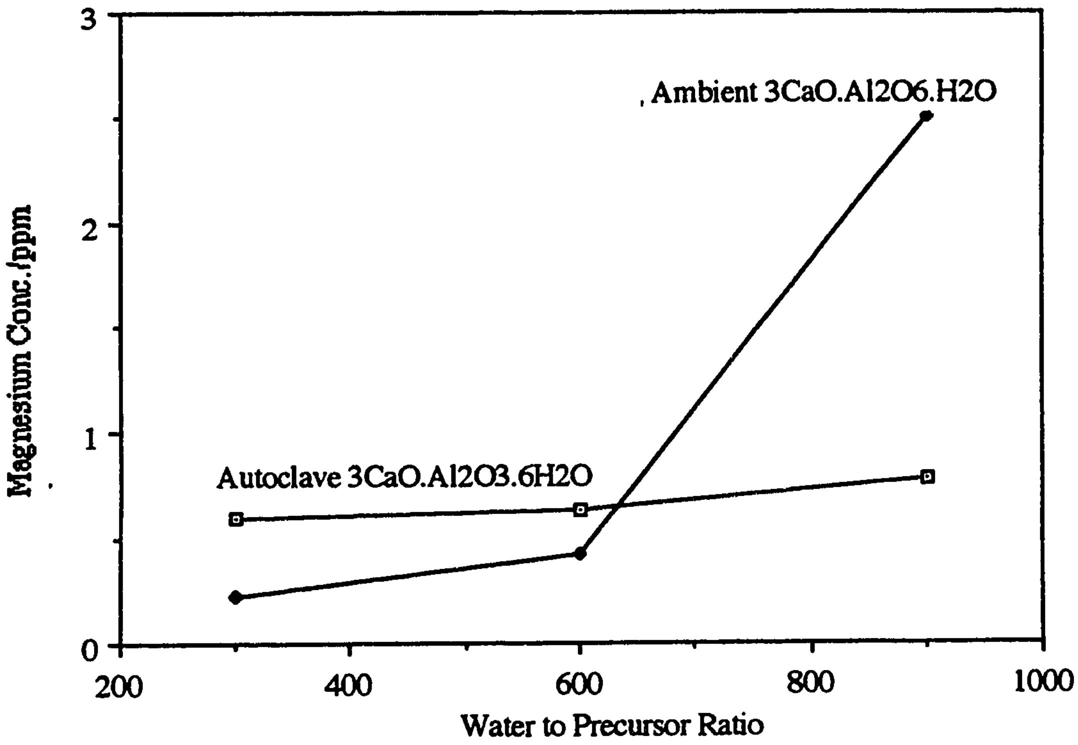


Figure 40. The Effect of Water to Precursor Ratio on Final Magnesium Concentration in Desiliconized Shell Produced Water using Autoclave and Ambient Prepared $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ precursor.

(Reaction Conditions: 85°C; 30 min;)

4.4 THE SOFTENING PROCESS

Figures 41 and 42 present the column break through curves for calcium and magnesium ion in the pretreated and desiliconized Shell water samples at water to precursor ratio of 900 using a hydrogen form weakly acidic cation exchange (100-200 mesh) resin. From these two figures it is observed that the resin can effectively soften the desiliconized water with a high regeneration efficiency. The combined total capacity of the resin for each step is shown in Table 11

Table 11

Total Exchange Capacities of the Resin During the Experiment

Experiment	Total Exchange Capacity of the Resin (meq/g)
Unreacted Resin (New)	11
Experiment 1 (Fresh)	7
Experiment 2 (1st Regeneration)	6.75
Experiment 3.(2nd Regeneration)	6.50

The reduction of the total capacity of the resin during the first experiment suggest the fouling of the resin by other compounds in the desiliconized water. The high content of sodium chlorides can be a contributing factor.in fouling. Although the resin was initially fouled to some extent, subsequent column regeneration did not result in significant additional reduction in exchange capacity. The resultant column efficiency of 60-64 % is quite satisfactory.

Furthermore the residual TDS of the desiliconized water was significantly reduced from 7500 mg/l to 900 mg/l during the polishing. This shows that a polishing step is important in the overall treatment process. The final dissolved aluminum content of the desiliconized water was also reduced from 1.3 ppm to 0.3 ppm after the ion exchange polishing. At this level of aluminum content, the formation of analcite [$NaAl(SiO_2)_2.H_2O$] scale in boiler tubes during recycling is very unlikely, thus addressing the concern over aluminum scaling. The residual hardness of the polished water before the break-through point was about 0.8 mg/l [$CaCO_3$]. This value is lower than the accepted value of 1.0 mg/l [$CaCO_3$] for steam generators in once-through boilers

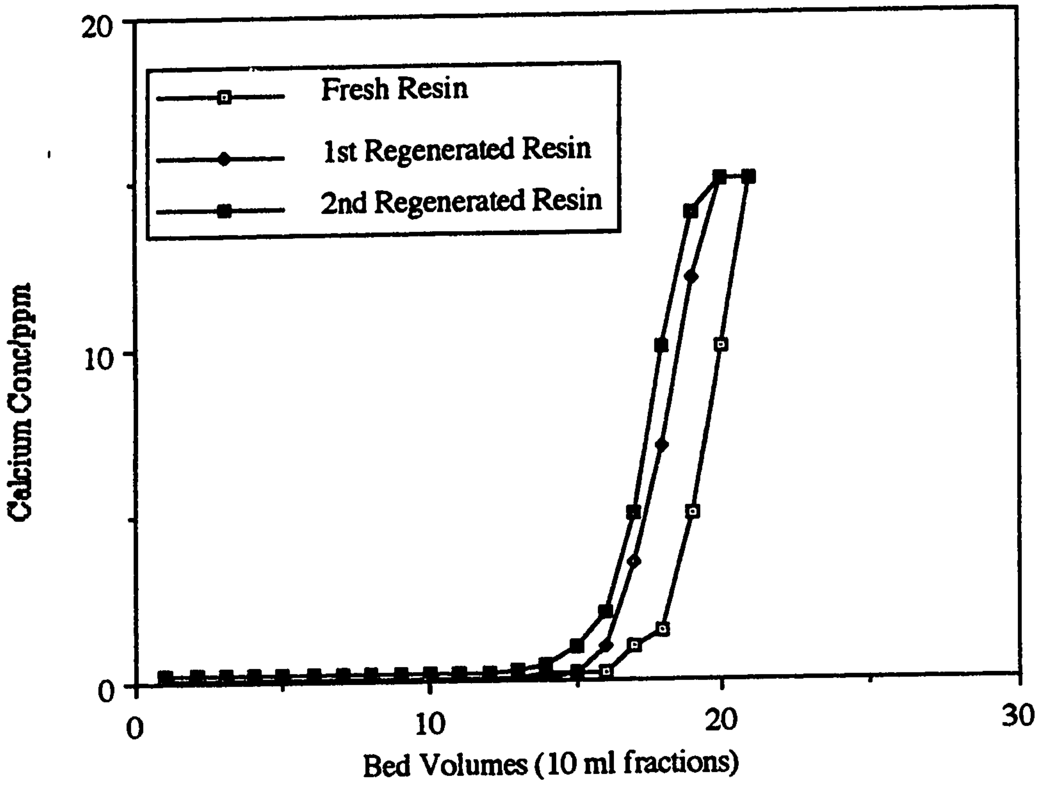


Figure 41. The Column Break-through Curve of Calcium in Pretreated and Desiliconized Shell Water at a Water to Precursor Ratio of 900 using Hydrogen Form Weakly Acidic Cation Exchange (100-200 mesh) (Resin Bed Volume = 140 cm^3

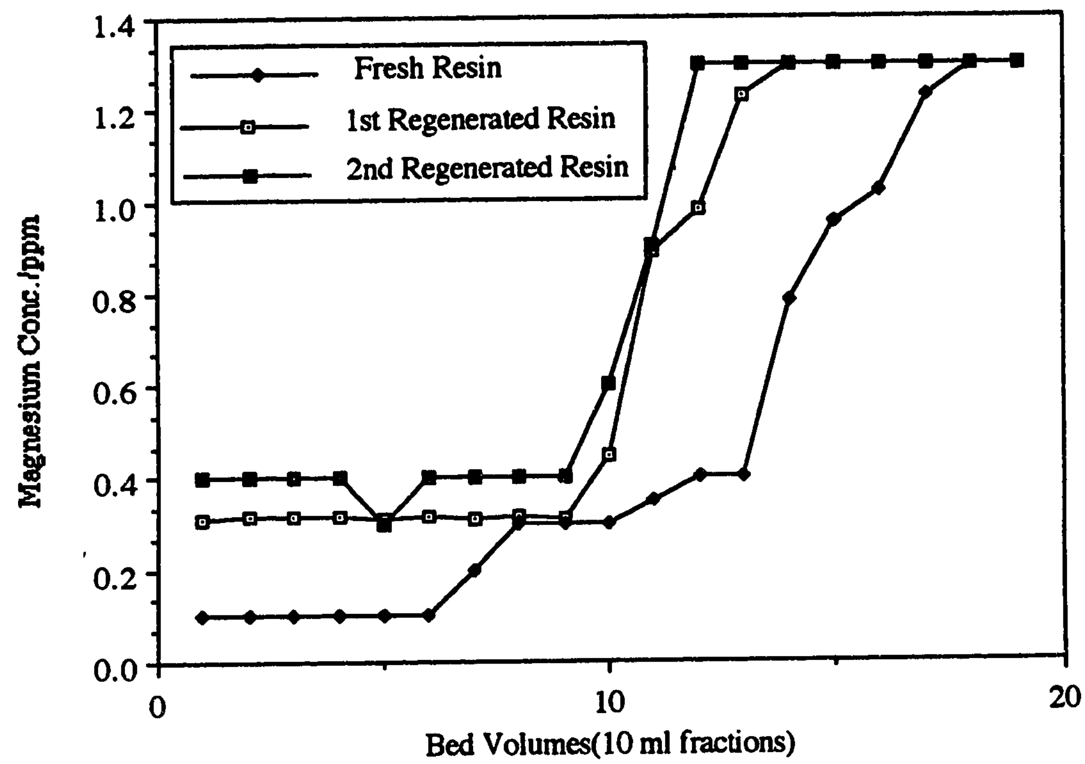


Figure 42. The Column Break-through Curve Experiment of Magnesium in Pretreated and Desiliconized Shell Water of Water to Precursor Ratio of 900 using Hydrogen Form Weakly Acidic Cation Exchange (100-200 mesh) (Resin Bed Volume = 140 cm^3

5.0. CONCLUSIONS

The removal of dissolved silica and silicates from Shell and Esso produced water sample was studied using the hydrogarnet process. Chemical analyses revealed that, the produced waters contained significant amounts of dissolved cation and anions such as sodium, calcium, sulphur, chlorides and silicates. The results of this study indicate that the hydrogarnet process, utilizing tricalcium hydroaluminate as precursor, is an effective method for silica removal from briny produced water. The presence of excess carbonate and bicarbonate ions makes the tricalcium hydroaluminate precursor less effective in the removal of silica from the produced waters due to partial dissolution. The results also reveal that, the removal of bicarbonate and carbonate ions is a necessary produced water pretreatment step before effective desiliconization can be achieved using the hydrogarnet process.

It can also be concluded that the hydrogarnet silica removal process is a fast reaction requiring a low residence time, even at ambient temperatures. The rate of desiliconization increases rapidly with increased temperature. Silica removal is accompanied by a simultaneous reduction in dissolved magnesium due to precipitation as magnesium hydroxide. Weakly acidic (carboxylic) ion exchange resin was found to be effective in the final polishing step for the removal of residual hardness, dissolved aluminum, and total dissolved solids reduction. Kinetics analysis indicate that the silica removal reaction is a pseudo first order reaction which is controlled by a physical phenomenon possibly associated with the diffusion of silicate ions from the bulk solution to the precursor surface.

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7.0 APPENDIX

DATA USED IN FIGURES

Figure 18

$Ca(OH)_2/Al(OH)_3$	Silica Concentration(ppm)	
	Esso	Shell
0.5	70.0	62.0
1.0	37.5	45.2
1.5	2.5	10.0
2.0	105.0	150

Figure 19

Time (min)	Silica Concentration(ppm)	
	Esso	Shell
0	239.08	221.96
1	148.2	146.0
5	145.1	145.1
10	48	135.0
15	0	146.0
20	0	140.2
25	0	142.0
30	0	142.0
35	0	146.0

Figure 20

Time (min)	Silica Concentration(ppm)	
	Esso	Shell
0	239.08	221.96
1	42.0	48.0
5	2.0	15.0
10	0	15.0
15	0	12.0
20	0	12.0
25	0	8.3
30	0	12.0
35	0	8.3

Figure 21

Time (min)	Silica Concentration(ppm	
	Esso	Shell
0	239.08	221.96
1	6.1	6.0
5	6.0	2.0
10	6.0	0
15	4.1	0
20	5.0	0
25	5.0	0
30	5.0	0
35	5.0	0

Figure 22

ln K	1/T x 10^{-3}
1.4	2.8
1.2	3.0
-0.3	3.2
-1.1	3.4

Figure 23

Time (min)	Magnesium Concentration(ppm)	
	Esso	Shell
0	5.8	7.1
1	5.1	6.35
5	4.57	6.25
10	4.85	6.15
15	4.57	6.25
20	4.87	5.90
25	4.65	6.0
30	4.67	6.25
35	4.78	5.75

Figure 24

Time (min)	Magnesium Concentration(ppm)	
	Esso	Shell
0	5.80	7.10
1	3.75	4.10
5	3.60	1.75
10	3.40	1.75
15	3.40	1.50
20	3.35	1.50
25	3.30	1.50
30	3.30	1.40
35	3.32	1.30

Figure 25

Time (min)	Magnesium Concentration(ppm)	
	Esso	Shell
0	5.8	7.1
1	1.90	3.2
5	1.30	0.8
10	0.90	0.75
15	0.80	0.75
20	0.60	0.60
25	0.55	0.50
30	0.5	0.50
35	0.45	0.45

Figure 26

Time (min)	Calcium Concentration(ppm	
	Esso	Shell
0	72.7	33.0
1	114.0	62.3
5	118.0	74.2
10	140.0	80.2
15	141.0	92.0
20	155.0	85.1
25	150.2	90.0
30	133.5	100.0
35	131.2	93.2

Figure 27

Time (min)	Calcium Concentration(ppm)	
	Esso	Shell
0	72.7	33.0
1	150.0	42.1
5	175.1	45.0
10	176.1	48.0
15	190.0	49.0
20	195.1	50.0
25	205.2	50.5
30	106.1	51.0
35	210.0	42.2

Figure 28

Time (min)	Calcium Concentration(ppm	
	Esso	Shell
0	72.7	33.0
1	175.0	35.0
5	180.0	37.0
10	195.0	48.0
15	190.2	43.2
20	220.0	48.0
25	228.0	47.3
30	238.0	46.2
35	237.0	48.0

Figure 29

Time (min)	Alumina Concentration(ppm	
	Esso	Shell
0	3.0	5.0
1	90.1	180.0
5	120.3	180.0
10	132.0	192.1
15	137.0	193.0
20	137.0	194.1
25	140.5	196.0
30	142.3	198.0
35	105.0	200.0

Figure 30

Time (min)	Alumina Concentration(ppm)	
	Esso	Shell
0	3.0	5.0
1	70.0	99.0
5	85.0	100.0
10	93.2	170.0
15	90.0	172.0
20	103.0	175.5
25	103.1	205.0
30	110.0	208.0
35	113.0	210.0

Figure 33

Water/Precursor Ratio	Silica Concentration (ppm		
	Untreated Water	Decarbonated Water-1	Decarbonated Water-2
300	6.8	3.4	9.5
600	124.2	4.5	7.5
900	172.2	37.	35

Figure 34

Water/Precursor Ratio	Magnesium Concentration (ppm)		
	Untreated Water	Decarbonated Water-1	Decarbonated Water-2
300	0.6	0.4	0.3
600	0.65	0.8	0.5
900	0.75	1.02	1.4

Figure 35

Water/Precursor Ratio	Calcium Concentration (ppm)		
	Untreated Water	Decarbonated Water-1	Decarbonated Water-2
300	26.8	100	130
600	20.0	75	110
900	13.0	15	110

Figure 36

Water/Precursor Ratio	Alumina Concentration (ppm)		
	Untreated Water	Decarbonated Water-1	Decarbonated Water-2
300	110	28.9	70
600	68.5	14.9	30
900	50.4	2.7	9

Figure 37

Water/Precursor Ratio	Silica Concentration(ppm)	
	Ambient Prepared $3CaO{\cdot}Al_2O_3{\cdot}H_2O$	Autoclave Prepared $3CaO{\cdot}Al_2O_3{\cdot}H_2O$
300	19.29	6.59
600	186.47	104.24
900	209.39	172.24

Figure 38

Water/Precursor Ratio	Calcium Concentration(ppm)	
	Ambient Prepared $3CaO{\cdot}Al_2O_3{\cdot}H_2O$	Autoclave Prepared $3CaO{\cdot}Al_2O_3{\cdot}H_2O$
300	248.26	26.80
600	25.86	9.52
900	10.64	7.54

Figure 39

Water/Precursor Ratio	Alumina Concentration(ppm)	
	Ambient Prepared $3CaO \cdot Al_2O_3 \cdot H_2O$	Autoclave Prepared $3CaO \cdot Al_2O_3 \cdot H_2O$
300	7.46	28.90
600	3.66	14.90
900	1.51	2.76

Figure 40

Water/Precursor Ratio	Magnesium Concentration(ppm)	
	Ambient Prepared $3CaO \cdot Al_2O_3 \cdot H_2O$	Autoclave Prepared $3CaO \cdot Al_2O_3 \cdot H_2O$
300	0.22	0.60
600	0.42	0.63

Figure 41

Bed Volumes	Calcium Concentration (ppm)		
	Fresh Resin	1st Regeneration	2nd Regeneration
1	0.1	0.1	0.2
2	0.1	0.1	0.2
3	0.1	0.1	0.2
4	0.1	0.1	0.2
5	0.1	0.1	0.2
6	0.1	0.1	0.2
7	0.1	0.1	0.2
8	0.1	0.1	0.2
9	0.1	0.1	0.2
10	0.1	0.1	0.2
11	0.1	0.1	0.2
12	0.1	0.1	0.3
13	0.1	0.2	0.5
14	0.2	0.2	1.0
15	0.2	1.0	2.0
16	1	3.5	5.0
17	5	7.0	10.0
18	5	12.0	14.0
19	10	15.0	15.0
20	15	15.0	15.0
21	15	15.0	15.0

Figure 42

Bed Volumes	Magnesium Concentration (ppm)		
	Fresh Resin	1st Regeneration	2nd Regeneration
1	0.1	0.31	0.4
2	0.1	0.32	0.4
3	0.1	0.32	0.4
4	0.1	0.32	0.4
5	0.1	0.31	0.3
6	0.1	0.32	0.4
7	0.2	0.31	0.4
8	0.3	0.32	0.4
9	0.3	0.31	0.4
10	0.35	0.45	0.6
11	0.4	0.89	0.9
12	0.4	0.98	1.3
13	0.78	1.229	1.3
14	0.95	1.30	1.3
15	1.02	1.30	1.3
16	1.23	1.3	1.3
17	1.3	1.3	1.3
18	1.3	1.30	1.3
19	1.3	1.30	1.3
20	1.3	1.3	1.3