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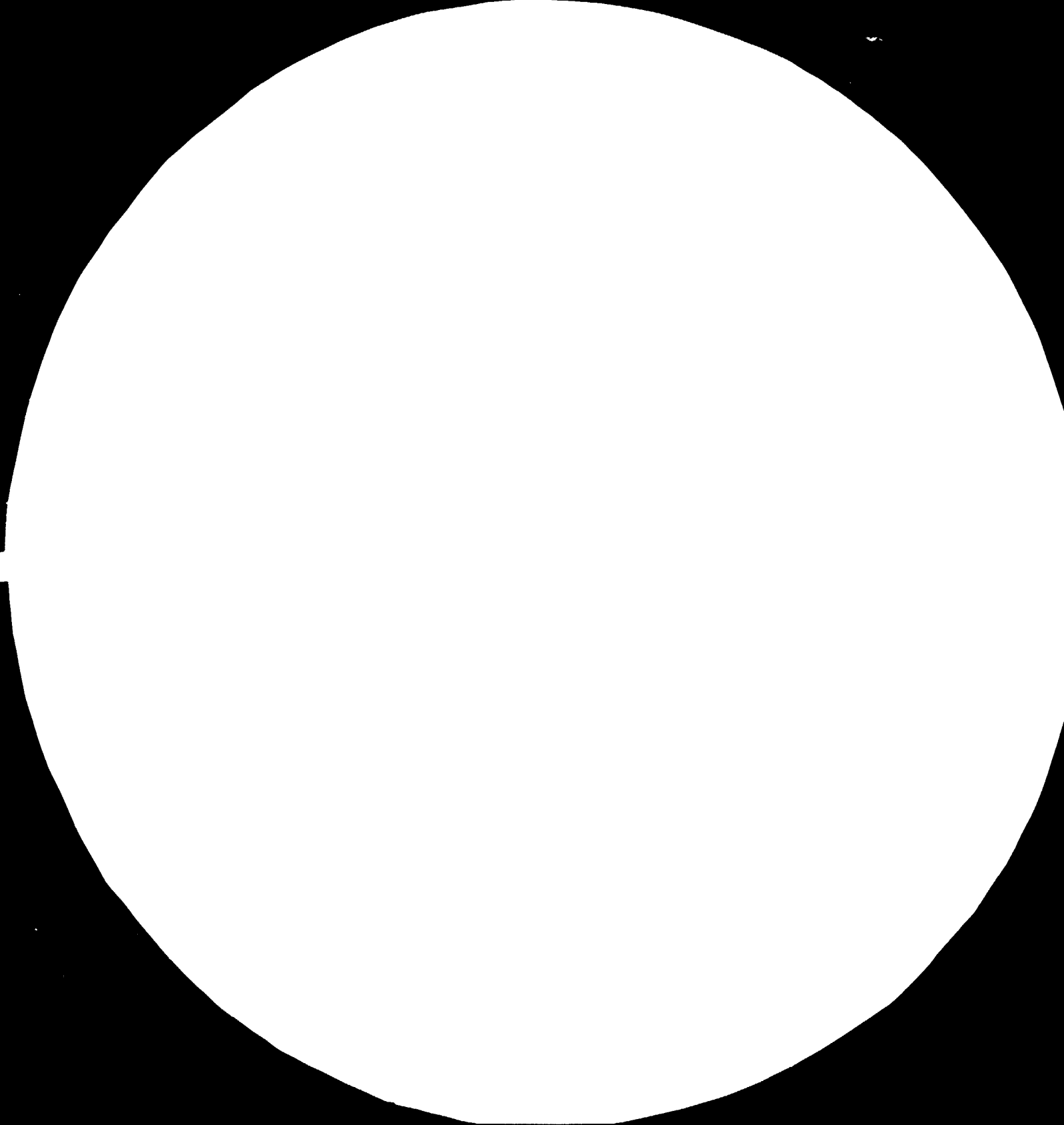
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9 August 1983

Ethiopia.

Preliminary Examination on the Viability
of Soda Ash Production from Brines
From Lakes Chitu and Shalla
Phase I.

Preliminary Report
SI/ETH/82/80

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This report has not been cleared with the United
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1. EXECUTIVE SUMMARY

- 1.0 This is an interim report of the expert's first of the three visits, for the pilot plant of the Soda project. Along with Ato Mekonen, he spent 10 days at the project site; an observatory was established at the Lake Shalla Bungalows. The rain-gauge has been calibrated so that it can be used with a 100 ml. (laboratory) measuring cylinder; details of work done at the site are given in Appendix 1.
- 1.1 After returning to Addis Ababa, more than 3 weeks were spent in the Laboratory, carrying out fractional crystallisation of Lake Chitu Brine, physical properties of brine (Sp. Gr. vs concentration and boiling points) have also been ascertained. Some experiments were carried out on preparation of Chemical Caustic Soda, using waste lime from acetylene plant. The results of these experiments are summarised in Appendix 2; methods of chemical analysis used are given in Appendix 3.
- 1.2 In section 2 are described all the Alkaline Lakes of Ethiopia, the three Crater Lakes near village Mega and near the Kenyan border (El Soda, Magado and Dillo) have much better concentration of solids than Lake Shalla and Lake Chitu. The total quantities of solids are, however, small and not of significance in the present context.
- 1.2.1 During a closer study of the important source of Alkaline brine for this project viz. Lake Chitu, it has been found that the area of the Lake taken in earlier studies is probably erroneous to the extent

of 300% reducing the resource to 5-6 years requirements (at 20,000 t.p.a. Soda Ash) from 15-20 years. A survey of the lake dimension will settle this point. If the lake area is 1.2-1.3 sq.Km. (as calculated from aerial photographs) instead of 3.7 sq. km. taken in earlier calculations more attention will have to be diverted to Lake Shalla than Lake Chitu. As Lake Shalla Brine concentration of Alkali is half that of Lake Chitu Brine, the size of the Solar Soda Works will become double. Concentration of flouride at Lake Shalla is also higher; reserves of Alkali at Lake Shalla are practically inexhaustible. Appendix 4 gives a comparison of reserves and replenishment at 4 important Lakes in the Great African Rift Valley viz Lake Magadi (Kenya) Lake Natron (Tanzania) and the two Lakes in the Lake District in Ethiopia.

In section 3 we have discussed the various processes applicable to recovery of natural Soda Ash from its various occurrences in the World. The process used at Searles Lakes in California, U.S.A. namely Carbonation of the Brine is not necessary as Lake Chitu (and Lake Shalla) Brine is less complex and is proportionally much richer in Alkali contents, A simpler and more economical process is recommended. This consists of fractional crystallisation through solar evaporation. The technology is known not only in Ethiopia but even within the National Chemical Corporation who has undertaken the pilot project.

1.4 In section 4, we have analysed the meteorological data obtained from Lake Chitu observatory through 11 months of observations in 1980 and correlated the data with meteorological data from nearby stations. It has also been recommended that we restart the observations immediately as we have most of the necessary instruments already with us.

1.5 In section 5, we have devoted some time to study the geothermal energy potential in the Lake District; Lake Bahalla and vicinity have indicated good potential for geothermal energy. The site being investigated at present by drilling wells (Lake Langano) is a little too far from our pilot project site (140 km by road).

It is suggested that investigations be made at Carbeti Caldera which is only 22-25 Km from Lake Chitu. Gas chromatograph, received recently by the Ethiopian Institute of Geological Survey may prove to be of benefit for the preliminary investigations of the site, which manifests geothermal activity through fumaroles and hot ground. A well drilled and found unsuccessful for power generation (being too small in output) could be used for the steam requirements for calcination and for Chemical Caustic Soda plant.

1.6 Section 6 deals with a diversification introduced in the project. Developing countries normally have larger demand for Caustic Soda than an equivalent quantity of Chlorine; for environmental and economic reasons, the size of the Electrolytic Chlor-alkali plant has to be limited to the genuine Chlorine needs (excluding such usage as dicalcium phosphate).

The balance of Caustic Soda needs could be met by conversion of Soda Ash to Caustic Soda. With a resource of natural Soda in brine form, one can use concentrated brine (at a certain density) instead of dissolving solid Soda Ash. Cost of such a brine, is a small fraction of the market price of Soda Ash and production of Chemical Caustic Soda can provide large profits for the project. Production of Caustic Soda also needs large quantities of steam and if ultimately, steam from geothermal sources is available, this would improve further the profitability of the project, such diversification is needed particularly if we have to switch over to Lake Shalla as the source, when Lake Chitu gets exhausted. Manufacture of Chemical Caustic Soda would also encourage rapid expansion of indigenous soap production from imported tallow and other indigenous oils.

1.7 Section 7 gives the design calculations of Solar Soda Works and the sizing of brine pumps and piping. Design of Solar evaporation pans is based on Meteorological Data (section 4) and experimental work in Lake Chitu Brine. Layout of Solar pans is given in Fig. 7 - 1. The basic data are summarised below:

<u>Solar Pans</u>	<u>Total area in Hectares</u>
3 condensing pans	6.4
1 Reservoir for sat. brine	1.4
2 Crystallisers	<u>0.8</u>
TOTAL	<u>8.6</u>
Main pump	50 m ³ /hr. Total head 18 m
Aux. pump	10 m ³ /hr. Total head 5 m.
Size of delivery pipe	125 mm, i. d. PVC.

1.8 Section 8 lists all the work to be done between expeditions first and second visits. It includes the odolite survey of the site, final selection of the site in the general area described in the report, purchase and installation of the brine pump, earthwork for the Solar evaporation pans, purchase and installation of PVC pipe, first filling of the Soda Works, taking observatory readings etc.; work items are listed for office work also such as obtaining previous survey drawing of Lake Chitu getting Lake Chitu Brine checked by the Central Laboratory (there is some serious errors in their earlier analysis); carrying out a market research on consumption of Soda Ash and Caustic Soda, (past and future), finding out through Ministry of Mines, resources of high grade limestone in the economic vicinity (100-200 Km.) of Lake Chitu.

Considerable Laboratory work has also been suggested for fractional crystallisation of Chitu Brine at 20-30°C. Some more work also has to be done on preparation of Chemical Caustic Soda, concentrate it to 28% NaOH and make soap out of the partly concentrated solution. Normally Chemical Caustic Soda is concentrated to 46-48% NaOH, but the higher concentration is achieved through evaporation in more expensive equipment using Nickel and Nickel alloys.

1.9 In section 9, implementation schedule is worked out. The schedule is worked out on the basis of taking advantage of the approaching dry season. All efforts should be made to complete the work by mid-October. This will require coordination and fast flow of funds. Earthwork may cost in the region of 250 to 300 thousand Birr.

- 1.10 In the last section, the plan of expert's second visit is discussed at what stage it would be most fruitful for him to come and a list is made of his activities. Depending upon the outcome of the investigations on the correct area of Lake Chitu, it may become necessary to carry out some Laboratory work on fractional crystallisation of Lake Shalla Brine.

2. Source of Soda and Reserves

2.0 The soda sources of Ethiopia can be divided into two groups viz. the three Crater Lakes of El Soda Magadia and Dillo near the Kenyan border and the two Lakes Shalla and Chitu further north. Lake El Soda is about 120 m in diameter and is saturated with alkaline salts but consisting in the main of sodium chloride and sodium sulphate. It has no visible spring to replenish the saline materials. The material is being exploited on a small scale. Lake Magado is being exploited on a small scale. Lake Magado is being fed by a spring with a salinity of 20,000 ppm. major constituent of which is sodium bicarbonate.

Flow of the spring water is 5,55 litres per second and annual replenishment is about 1800 tons for sodium bicarbonate. The lake water has a tds content of 188,000 ppm. The total contents of alkali in the lake comes to an equivalent of 67,000 tons sodium carbonate, in a total of 147,000 tons of solids. Lake Dillo is entirely covered with a one cm thick crust underlain by multicoloured slime (algae) beneath the slime is a black water-logged mud. Analysis of salt crust varies from place to place but the major constituent is sodium sulphate. There is a spring which feeds this small lake. A decade ago in a report prepared by a German Firm, these three Greater Lakes were given higher priority for exploitation than Shalla and Chitu. In todays context, the reserves in these lakes appear in significant.

2.0.1 The major sources of soda in Ethiopia are the two Alkaline Lakes, Shalla and Chitu, in the Ethiopian Rift Valley. The Rift Valley is the most extensive rift system on the

earths continents, running some 400 km from the Zambazi River in Mozambique to the Afar Depression and Red Sea. It was named by the British Geologist John Gregory in 1893. In Ethiopia the Rift extends over 1000 km in a general North-Northeast direction from the Kenyan boarder. The main Ethiopian Rift averages about 80 km wide.

The central part of the rift is as symmetrical both morphologically and stratographically the lowest parts of the floor lie close to the eastern escarpment and are occupied by seven large lakes to tectonic or volcano-tectonic origin. From north to south, they are as shown in Table 2.1

Table 2.1

<u>Lake</u>	<u>Level Above Sea Meters</u>	<u>Depth Meters</u>
Zwai	1650	7
Abiata	1575	14
Shalla	1570	257
	-	-
Awasa	-	-
Abaya	-	-
Shamo	-	-

Lakes Shalla and Awasa have no outlets but Lake Awasa must have a rapid turn-over losing water by underground seepage, because its waters are not highly mineralised Lake Shalla receives fresh water overflow from Lakes Zwai, Langano and Abyata.

- 2.0.2 The levels of all lakes have been higher in recent past. dating of shells (by carbon - 14) from lacustrine deposits 1.5 km east of Shalla and about 58 meters above the lake 5610 + 100 years before the present. Lacustrine beds 84 m. above Lake Shalla: 1.75 km east, are 9220 + 190 years before. The highest recognized terraces of the Lake District are about 130 m. Above Lake Shalla near Lake Zwai and 110 - 120 m above Lake Shalla on its western Shore. It is claimed that this level corresponds to an overflow channel into the Awash Basin. It also corresponds to the present level of Lake Awasa, but it some tens of meters lower than the divide between Awasa and Shalla.
- 2.0.3 Lake Shalla's longest axis is approximate normal to the strike of regional faults, whereas all other lakes are elongated north-east parallel to the regional faults. This explains the exceptional depth of the lake and it is believed that Lake Shalla occupied a major volcano-tectonic collapse modified by regional faulting. The area deeper than 250 m. forms abroad "figure 8" shaped area close to the south shore.
- 2.0.4 Lake Chitu 1 km in diam. and about $1\frac{1}{2}$ km. south of Lake Shalla occupies a basaltic tuff ring. Initially, eruptions were subaqueous but in the later stages, sub-aerial. Afterwords the crater filled with water to approx. 15 - 20 m. above present lake level.
- 2.1 Chemical Composition of Waters from Lake Shalla and Lake Chitu.
- 2.1.0 Lake Shalla: we have two sources of analysis viz.
a) Laboratory of Geological Survey of Ethiopia and reproduced by Mr. Du Bois and b) sampled and analysed by U.N. team of experts in 1975 (Investigations of Geothermal resources for Power Development (Ethiopia)).

2.1.1 For Lake Chitu, we have two sources for complete analysis and one more for major important constituents. These are a) Laboratory of Geological Survey b) sample analysed in June 1983 by the Central Laboratory and Research Institute. of Ministry of Health. Sample which was sent to the Central Laboratory has also been analysed under the supervision of the Soda Ash Expert in the laboratory has also been analysed under the supervision of the Soda Ash Expert in the Laboratory of National Chemical Corporation using methods described in appendix 3.

The results are presented in Tables 2.2 and 2.3

TABLE 2.2

Chemical Composition Lake Shalla Water

Parts Per Million

<u>Constituent</u>	<u>Source a</u>	<u>Source b</u>
PH	9.7	10.15
Ca	6	Less than 3
Mg	1	" " 2
Na	7100	6800
K	254	225
CO ₃	3690	4080
HCO ₃	4392	4387
Cl	2982	3030
SO ₄	133	137
F	100	300
Br	23	not determined
I	0.3	0.05
SiO ₂	126	116
HBO ₂	40	98
Li	-	0.05
Ni ₄	-	1.18
H ₂ S	-	1
Total	18847	19180
Total cations equiv.	315.5	303
" anions equiv.	292.4	318

Table 2.3
Chemical Analysis of Lake Chitu Brine
Part Per Million (mg per litre)

	<u>Source A</u>	<u>Source B</u>	<u>Source C</u>
PH	9.8	10.2	
Constituents			
Ca	5.01	1.0	-
Mg	0.61	not det.	-
Na	34000	14900	-
X	1056	980	-
CO ₃	12400	10758	13839
HC ₃ O ₃	1650	5,112	3296
Cl	7285	5,900	5964
SO ₄	305.6	396	-
F	250	89	-
Br	3.99	0.6	-
I	1.30	0.6	-
Total	56,958	38,203	37,340
Total Cations Eq.	1505.7	673	-
" Anions Eq	665.1	622	-

There is some serious error in the analysis made by the central Laboratory and as we are vitally interested in the analysis of Chitu Brine, we should ask them to repeat the analysis. A sample may also be sent to the University for complete analyses.

2.2 The Reserves:

2.2.1 Lake Shalla: According to earlier reports, the Eastern portion of the Lake has a surface area of 198 sq. km. and average depth of 164 meters. The volume of Lake water in the Eastern portion comes to 32.472×10^9 cu. meters.

The smaller western remainder of the Lake covers 99 sq. km with an average depth of 70 meters. The volume of Lake water in this portion comes to $6,93 \times 10^9$ cu meters.

The total volume is thus 39.4×10^9 cu. meters.

Taking an average of the two analyses given in Table 2.2 the total alkali expressed as Na_2CO_3 comes to
10,577.4 pp, Na_2CO_3
or 10.6774 kg per $\text{m}^3 \text{Na}_2\text{CO}_3$

The total alkali content of the whole lake is
 $39.4 \times 10.6774 \times 10^6$ metric tons
or 420.7 million tons

2.2.2 Lake Chitu: There is some doubt about the area covered by this lake; according to the description given by the U.N. Team on Geothermal Investigations (1973), the lake is about 1 km in diam. giving an area of about 0.79 sq. km. According to Sheet 073802 series Eth 4 (Dept. of Overseas Survey) Edition 1976, the lake is 1300 m. long and 750 m wide at its widest portion. Estimation of area made by the Soda Ash Expert from this map gives a value of about 0.93 sq. km Du Bois Report gives the area as 3.7 sq. km, Topo Sheet NB 37.2 series E.M. 5 (1979 Edition). although on a smaller scale (1:250,000 against 1:50,000 for 0738 02) tends to confirm the lower area value. For the calculations of reserves we have for the present taken the Du Bois value, but as this is of vital interest to us, we should get survey report made by Ato Alazar of the Ministry of Mines to the Ministry of Industries.

Taking an area of 3.7 sq. km and the alkali contents based on our own analysis (27.313 kg per cu. m. as Na_2CO_3), and 8.5 meter depth the total alkali reserves come to $3.7 \times 10^3 \times 8.5 \times 27.313$ metric tons or 859,000 tons.

2.3

Replenishment of reserves: for any reserves of this nature, it is difficult to estimate the replenishment of the reserves through alkaline springs and other natural processes. For one thing all the alkaline springs surrounding the lake may not have been analysed and their flows measured. Then there may be a number of springs which deliver the alkaline water to the lake through underground flow. Then again, as in case of Lake Magadi, in Kenya, there could be internal recirculation and the input may not be all original. In case of Lake Magadi, which has been studied in great detail the gross input through alkaline springs have been estimated at 1.5 million tons of sodium carbonate annum, but the net input after deducting for recirculation through deep underground reservoir, comes to only 1/3 of the gross. The gross replenishment from visible springs have been estimated in Table 2.4 below; this is based on flows and analysis recorded by U.N. Teams on Geothermal Investigations (1973).

Table 2 - 4
Replenishment of Alkali Through Visible Springs
Lake Shalla

<u>Spring No.</u> <u>NB 37/2</u>	<u>Total CO₃</u> <u>Content ppm</u>	<u>Flow</u> <u>Litres/Sec.</u>	<u>Tons Na₂CO₃</u> <u>Per year</u>
29	726	1.2	49
30	1667	33.3	33093
31	326	4.5	82
33	1033	0.5	29
35	912	-	-
36	1056	-	-
90	2304	0.1	13
91	3442	3.0	575
87	1251	5	364
88	1206	6	403
60	1166	6.6	429
Total			5.037

The largest contribution is by spring 30 which is also the hottest spring (boiling temp.) (see also Appendix 1).

The visible replenishment quantum for Lake Shalla is quite low but in the present context, it is not of importance as the reserves are very large (e.g. Lake Natron in Tanzania has a reserve of 136 million tons alkali as against 421 million for Lake Shalla). Again, it is considered possible that Lake Shalla may overlie evaporite deposits.

- 2.3.2 As regards replenishment factor for Lake Chitu, springs 61 to 69 emerge from the sediments close to lake level on the east through south-east to south shores; temp. are between 45 - 60°C and total visible discharge 6 litres per second. Spring 65 is the largest (60°C, 3.3 litres per second) and contributes 180 tons Na₂CO₃ per

year to the Lake. This is quite insignificant. As the reserves are also small it would be necessary to watch closely the lake levels, the brines are pumped out for exploitation. There is a possibility that Lake Chitu may be getting brine from Lake Shalla through underground connection. A level gauge may be fixed up near the pumping installation and after pumping is started, regular reading may be taken for the level.

2.3.3 Appendix 4 gives the comparison of the Four Alkaline lakes in the African Rift Valley.

3. PROCESSES FOR SODA RECOVERY.

3.0 Based on phase rule and solubility considerations there are a number of processes which can be employed for recovery of Soda Ash from multicomponent systems such as the brines from Lake Chitu or Lake Shalla. These processes will be reviewed in brief, before making a selection applicable to our conditions, but before we discuss the various processes used in commercial practice or which are theoretically possible, we should discuss the composition of Lake Chitu and Lake Shalla Brine and compare it with other brines from which Soda Ash is recovered.

3.0.1 The most important impurities in the two brines are Na_2SO_4 and NaF the best way to quantify these impurities is to express them as ratios. Table 3.1 expresses these impurities as ratios for the two lake brines and compares them with many other alkaline brines. The values immediately bring out the complexity of the separation processes.

Table 3.1 Comparison of Brines from Alkaline Lakes.

SOURCE	CL	SO ₄	F
	Total CO ₃	Total CO ₃	Total CO ₃
Lake Chitu	0.632	0.0156	0.0075
Lake Shalla	0.629	0.0105	0.0057
Lake Natron (subsoil)	0.144	0.0305	0.0040
Lake Magadi (Kenya)	0.474	0.00872	0.0250
Lake Hannington (Kenya)	0.282	-	0.0029
Searles Lake	4.53	1.66	"

From the above table, it is clear that Searles Lake Brine is different in nature from the Brines in the Rift Valley. The higher the ratio in any one of the three columns, more difficult it would be to separate out the desired Carbonate by simple fractional crystallisation. Sodium Carbonate, normally, has a higher solubility than Sodium chloride and would separate out first, but if the concentration of Sodium Chloride is high to start with, it is this salt that separates out first. Between Lake Chitu and Lake Shalla Brines, there is concern. Sulphate impurity is less in Lake Shalla Brine but Fluoride is much higher. Fluoride Solubility in Alkaline Brines containing Sodium Chloride is very low and NaF begins to separate out quite early if its concentration is high if we have to use Lake Shalla Brine in future, this problem will need examination. The relative contents of F⁻ is higher than in Lake Magadi and at Lake Magadi, Fluoride has been a problem from time to time. We have however, selected Lake Chitu Brine for the reasons of its better concentration and until this source gets exhausted the question of use of Lake Shalla Brine may not arise.

- 3.1 Coming now to the process alternatives quite a number of processes have been developed for recovery of natural Soda Ash, in U.S.A., Mexico and elsewhere. Most of these processes, relate to recovery of Soda Ash from solid trona, which occur in Wyoming, (Green River Valley) USA, Lake Magadi (Kenya) Lake Natron (Tanzania) and elsewhere. These processes are naturally not applicable in our case. Searles Lake in USA recover Soda Ash (and a number of other Chemicals) from brine which is already at saturation with a number of salts. The processes

used there are not applicable to our case mainly because, as shown in Table 3.1 the composition is very different from the Alkaline Lakes in the Rift Valley here. If Searles Lake Brine were concentrated further it would be NaCl (Common Salt) which would separate it first and not the Sodium Carbonate, as in our case, for this reason, they use an expedient of converting Sodium Carbonate to Sodium Bicarbonate which decrease the solubility and the Alkali is separated as Sodium Bicarbonate to be converted to Soda Ash subsequently from the Searles Lake upper reservoir, the process used is different. The Sulphate content here is and Burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$) is crystallised out, Na_2CO_3 separated subsequently as Monohydrate, and then calcined it should also be remembered that is Searles Lake Brine, Na_2CO_3 is the fourth in order of magnitude in the composition and that the brine is much more complex (with two major actions Na and K, instead of one).

- 3.1.1 The first step in recovery of Soda Ash from our Lake Brines, in every case, has to be concentration. This can be achieved by evaporation in multiple-effect evaporators or by Solar evaporations. Even if geothermal steam were available (see section 5), the cost of multiple effect evaporating equipment would be quite high. There would be some scaling problems too. Undoubtedly, the choice for the preconcentration (upto the stage of crystallisation) would be by Solar ponds.
- 3.1.2 after the brine reaches the saturation (about 22°Be), the alternatives could be either by further concentration and fractional crystallisation in Solar ponds or in a multiple effect crystallising evaporator or evaporator followed by a crystalliser. In Solar ponds, the "equipment"

cost is small but quality control is more difficult, for one thing, there is no control of temperature at which crystallisation is carried out. The solubility of Sodium Carbonate varies appreciably with temperature whilst the solubility of Sodium Chloride (the major impurity in our Brines) hardly changes with temperature, we cannot take advantage of this in Solar ponds fractional crystallisation, as in case of multiple effect evaporation/crystallisation. Another factor is the contamination with soil during harvesting of product from Solar ponds for these reasons, we have to keep in mind, the alternative process and closely watch the development of geothermal energy (see section 5).

- 3.1.3 From the limited work (due to time limitation) done in the Laboratory (see App. 2) it seems possible to set an acceptable product (for the local market) by fractional crystallisation and washing the harvested product by Chitu Brine of 22° Be, and unconcentrated Chitu Brine in two steps. If a higher quality product is desired (for export), a part of the production can be treated further. It can be dissolved in hot water and the saturated solution put through a crystalliser (Swenson-walker of similar type) and fractional crystallisation carried out at a higher temperature. The mother liquor can be reused partly and fed back to Solar ponds partly, to avoid loss of Sodium Carbonate.

4. METEOROLOGICAL DATA

4.0 For Solar Evaporation the design of Solar Soda Works would depend upon the meteorological parameters. National Chemical Corporation have taken meteorological data for 11 months in 1980 (From Feb. 1980 to Dec. 1980). The average monthly results are given in Table 4.1.

Table 4.1 Meteorological Data for Area between Lake Shalla (SW) and Lake Chitu 1980.

1980	Dry Bulb t°C	Wet Bulb t°C	Relative Humidity	Wind Km/hr	Evaporation mm/day		Rainfall mm.
					Measured	Calculated	
Feb.	25.8	16.5	39	9	6.9	11.6	15.6
March	26.5	17.3	38	9	7.8	12.5	-
April	26.6	19.9	55	8.9	8.1	9.2	30.4
May	26.4	18.1	45	8.3	6.3	10.4	80
June	23.5	17.8	58	9.3	48	8.6	60
July	22.6	16.3	52	10.3	5.0	8.2	36
Aug.	22.7	17.2	58	8.8	5.1	6.7	50
Sept.	23.6	17.7	52	7.2	5.4	7.6	50
Oct.	25.3	16.3	38	9.4	7.9	12	10
Nov.	24.6	15.2	38	10.6	8.0	12	-
Dec.	24.3	14.	40	6.5	8.1	9.7	-

4.1 Soda Ash Expert has also compiled data for the general area of Lake Shalla/Lake Chutu from meteorological maps, published by Ethiopian Meteorological Service(1979). The data compiled are given below in Table 4.2

Table 4.2 generalised Meteorological Data for Lake Shalla/Chitu area (Several years average upto 1978).

Average Several years	Mean Max. temp. °C	Mean Min. temp. °C	Monthly rainfall mm	Mean Monthly Hrs Sun-shine	Mean R.H% at Noon	Mean Daily Evap. mm		
						Awassa		
						1973	1974	1982
Jan	30	10	25	275-300	40	7.0	8.7	-
Feb.	30	10	50	250	30+	9.3	9.1	-
March	30	10	50	250	40	11.4	6.4	-
April	30	15	100	225	40	7.2	8.6	4.7
May	25	15	100	250	50	4.2	4.4	4.9
June	25	15	100	225	60	4.5	3.9	4.4
July	20	15	150	150	70	2.8	3.4	4.0
Aug.	25	15	150	150	70	2.7	3.4	2.3
Sept.	25	15	100	150-175	60	2.8	2.7	2.8
Oct.	25	10	50	250	50	4.1	4.8	5.3
Nov.	25	10	10	275	50	6.9	7.6	5.6
Dec.	25	10	10	275	50	8.1	8.1	5.9

4.1.1 Data compiled from meteorological maps as given above (except specific data on evaporation rates given in last 3 columns) have to be used with caution, for one thing, the intervals between the lines Isotherms or Isohyets are large. For another, particularly for rainfall, it depends upon how far the nearest data collection centre is. Rainfall often varies considerably from place to place within a few km. distance. For example, in the annual rainfall, Lake Langano comes

within 400 mm isohyest and is immediately surrounded by an isohyest of 1200 mm. Lake Shalla Abayata and major part of Lake Zwai come within isohyest of 800 mm. It is possible that if data are available from an additional station, such as ours at Lake Chitu, an additional isohyest can be constructed. During Expert's limited stay at the Lake site (for 10 days) it was observed at least on 3 occasions that rainfall at our observatory site was distinctly less than rainfall at 5-7 km. away on Southern side.

4.2 The most important parameters of meteorological nature for design of Solar Works are rainfall, number of rainy days, and evaporation. The most reliable evaporation data for us are by pan evaporation method. All these data can be collected right away, as we have the necessary instruments. The available raingauge has been calibrated so that the person concerned will have to be given only a 100 ml. measuring cylinder from our Laboratory. For pan evaporation readings, only a scale is necessary. Construction of a smaller pan (from g.i. sheets) of about 15 cm diam. or 12 x 15 cm rectangular size is advisable to avoid wave action and necessity to take more than one reading at a time.

4.2.1 As regards the rainfall data, the data collected from Meteorological maps are too general to be of direct use for detailed calculations of Solar pond area, we will have to rely on our own limited observations made during 11 months (which again are of limited value for rainfall data which should be averaged over a number of years).

4.2.2 For evaporation rate, comparison of data collected by us with data for Awassa and 9 months data for Mitto obtained from Ethiopian Meteorological Service reveal that data for Awassa are more applicable to us than for Mitto. Data collected by us in our observatory are of the same magnitude for Awassa for February, April and December, for the month of March and May, our measured rates are slightly lower. For the months of June to November, we are getting better evaporation than Awassa. For the design of pilot Solar evaporation works, we shall therefore, use the average evaporating rates for 2 years of Awassa and 11 months of our own observations. These average rates, taken for design purposes are given in Table 4.3 below.

Table 4.3

Mean daily evaporation rate average for 2 years for Awassa and 11 months for Lake Chitu

Month	Mean Daily Evap. mm	Monthly total mm	Annual
Jan.	7.85	243.4	
Feb.	8.43	236.0	
March	8.53	264.4	
April	7.97	239.1	
May	4.97	154.1	
June	4.40	132.0	
July	3.73	115.6	
Aug.	3.73	115.6	
Sept.	2.63	108.9	
Oct.	7.50	173.6	
Nov.	7.50	225.0	
Dec.	8.10	251.1	
		Total	2258.8

4.2.3 Evaporation rate using a Colorado type of pan (this is the usual pan method) differ somewhat from actual evaporation rate from large free surfaces. The Chitu Solar pans will be situated near large open water surface (Lake Shalla) and may be somewhat lower. As the observatory readings are near the large open surfaces of the Lakes (Awassa in one case and Shalla in the other) no correction may be necessary. (The correction factor is usually 0.83) It is interesting here to note that annual evaporation rate on the Ethiopian Plateau is a function of altitude, as shown by the following table.

Table 4.4
Evap. Rates for Large Water Surface

<u>Station</u>	<u>Altitude meters</u>	<u>Mean Annual Evaporation mm</u>
Addis Ababa	2408	1,407
Koka	1592	1,751
Zwai	1625	2,000
Wonji	1540	2,227
Metahara	955	2,946
Awora Melka	805	2,855
Lake Assal	150	4,800

Our Solar pans are at a level of approx. 1570 meters and the annual average we are taking (Table 4.3) viz 2258.8 mm generally agrees with the above data.

5. GEOHERMAL RESOURCES

- 5.0 It is a fortunate coincidence that in the region where we have the Soda resources, there are indications of intense geothermal activity; such activity is observed, though on a much smaller scale at Lake Natron and Lake Magadi too. At Lake Langano, about 140 km by road from Lake Chitu site, drilling of one well has already been completed and drilling of a second well has been started. The permeability of rock in the bottom of the first well may prove to be too poor for commercial exploitation (min. 15 kg. per second steam output). It is however, possible for us to make use of an unsuccessful well. Direct use of steam is more economical than its conversion to power.
- 5.1 Because of these possibilities of finding geothermal energy and using it in the project, a visit was paid to the Lake Langano drilling site and discussions held with Mr. Roy Johnstone at the drilling site (see Appendix I). The Soda Ash Expert also had discussions with Mr. Hagen Hole, Chief Technical Advisor of the Geothermal Project, Ato Ababa, Project Manager and Ato Getahun Damissie, General Manager, Ethiopian Inst. of Geological Survey.
- 5.2 In the regions where there are hot mineral springs, the temperatures underground (for geothermal activity) are predicted by geochemical investigations. With fumaroles one needs Gas Chromatographical Investigations; fortunately the Inst. of Geological Survey have recently received the Gas Chromatograph and this will be of use in investigating the geothermal activity in Corbetti Caldera.

5.3 Depending upon the contents of water (free moisture as also water of crystallisation) we have to transport 1.6 to 2.0 tons material (harvested soda crop) per ton of Calcined Soda Ash. (It is more economical to transport solid material to the source of steam than the other way). It is therefore, necessary to find a source of steam as near to Lake Chitu as possible, as mentioned above, Lake Langano site is about 140 km by road from Solar Pond site.

5.3.1 Corbetti Caldera site is only 20-25 km. from Lake Chitu. This site is in the region of Chebbi Volcano ($7^{\circ} 10' N$ and $38^{\circ} 27' E$)*. (Word Chebbi comes from *Araei*. Galla word meaning obsidian). Corbetti Caldera, just north of Lake Awassa, is a sub-circular volcanic depression 10-15 km. in diam.

The main Hydrothermal activity within the region is manifested by hot ground and hot vapours. The inhabitants cover the vents with vegetation to condense the steam for drinking water. The most important manifestations occur at Demo Argo. A 250,000 m² of the area is hot, innumerable fumaroles (temp. upto $91^{\circ} C$) exist. About 2% of the total area of hot ground exceeds $85^{\circ} C$ at 15 cm. depth. Hot ground and fumaroles occur at several places between Corbetti Caldera and Lake Shalla. At Doredimtu, north of Corbetti Caldera about 16,000 sq. m. area is warm and there are weak fumaroles.

5.4 The original idea of investigation; Corbetti Caldera by drilling wells (subsequent to Gas Chromatographical Investigations) is not given up. The question of priorities will arise in due course. Ministry of Industries should take up this matter appropriately with Ministry of Mines for investigating this field. Our requirements of steam are given in the following

5.5 Steam requirements for Lake Chitu Chemical Project;

5.5.1: Low pressure steam

Quality: Saturated

Pressure: 5 to 6 atm. abs.

Quantity: For evaporation of saturated Chitu Brine for crystallising Sodium Carbonate (alternative route)

12 tons per hour for 20,000 tons Soda/year
Chemical Caustic Soda 19,000 tons/year.

10 tons per hour.

Total 22 tons per hour.

5.5.2: Medium pressure steam

Pressure: 10-12 atm. abs.

Quality: Superheated: 5° above saturation

Quantity: 0.7 ton per hour.

5.5.3: High pressure steam.

for calculation of Soda Ash: (20,000 t.p.year).

Quality: Saturated Pressure 28 atm. abs.

Quantity: 5 tons per hour.

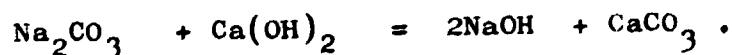
To summarise, total steam requirements

Pressure Atm. Abs.	Quality	Quantity Tons per hour
5 - 6	Saturated	22
10 - 12	5°C Superheat	0.7
28	Saturated	5.0
Total		<u>27.7</u>

6. PRODUCTION OF CHEMICAL CAUSTIC SODA

6.0 Consideration is being given to the production of Caustic Soda for some time now. The process considered is by electrolysis, with the simultaneous production of Chlorine. To the extent of genuine demand for Chlorine (for bleaching in Textile and other industries, Water Purification etc.) it would be advisable to put up an Electrolytic Chlor-alkali Plant, using the Membrane type of Electrolytic Cells, which produces high grade Caustic Soda not needing further concentration for most of its applications even a small sized plant with partial or full use of Chlorine at site, is economical. Normally, taking only genuine demand for Chlorine, such a plant does not meet the full requirements of the Caustic Soda needs of the country the balance of requirements of Caustic Soda then, have to be met by Chemical Caustic Soda Production.

6.1 In this process, a solution of Soda Ash is taken and reacted with Calcium Hydroxide Slurry (prepared from washings obtained in the process). A large part (over 85%) of the Soda Ash gets converted into Caustic Soda by the following reaction.



the reaction is carried out nearly at boiling temp. to get higher conversion efficiency. The slurry is then settled in continuously working Dorr-type thickeners and the Calcium Carbonate mud is washed counter currently

in a series of settlers. The washings are used for dissolving Soda Ash (where solid Soda Ash is used) and for preparing milk of lime. The clear liquor is concentrated to 46-48% NaOH in multiple-effect evaporators cooled to separate unconverted Soda Ash and other salts (NaCl and Na_2SO_4). Sodium Sulphate has to be added, if not already present in sufficient concentration to ease the separation of Na_2CO_3 and NaCl.

6.2 Soda Ash Expert is recommending the use of this process for the Lake Chitu Project because, we can use Chitu Brine at a certain concentration, directly from the Solar ponds for conversion to Caustic Soda, in many developing countries, including India, where Chemical Caustic Soda is made, the major cost item is Soda Ash solution obtained from a decarbonator, where Soda Ash is made in solution from, by wet decomposition of Crude Sodium Bicarbonate. This solution of Sodium Carbonate is somewhat cheaper than dry Soda Ash, but cost-wise, Chitu concentrated Brine would cost only a small fraction of such soda solution in a Synthetic Soda Ash plant, with such an obvious advantage in the cost of the main raw material (the other raw material being lime). The production of Caustic Soda by this process will prove to be attractive.

6.3 As regards the concentration of Soda Solution to be taken for Causticisation, this depends to some extent on the costs of raw materials and energy. Higher the

concentration of Na_2CO_3 in the starting solution lower is the conversion efficiency, but this also brings down the consumption of steam for concentration of Caustic liquor. A balance is struck depending upon relative costs of Na_2CO_3 and steam.

- 6.3.1 The concentration of Na_2CO_3 found best when Soda Ash costs are high, is given below.

$$\left. \begin{array}{l} \text{Total } \text{Na}_2\text{CO}_3 \\ \text{Uncl } \text{NaHCO}_3 \end{array} \right\} \text{--- } 238.5 \text{ G.P.L.}$$

This corresponds to Chitu Brine concentrated from 8 Vol. to 1 Vol. or a TDS of nearly 300 gpl. (some solids would have separated out at this stage, mostly Sodium Bicarbonate and some Sodium Carbonate also). In order to have a richer source of Na_2CO_3 , it would be best to start causticisation with Chitu Brine at 22°Be , using washings from the process to slake burnt lime.

- 6.4 We have conducted some preliminary experiments on Causticisation of 1:4 Chitu Brine using lime slurry detained from Acetylene Plant in Addis Ababa. (see App. 2). A large sample of the slurry has been dried in the oven and sampled and analysed further experiments can be carried out with this lime sample. (13.1 grms. are needed for Causticisation per 100 ml. of 1:4 conc. Chitu Brine.

7. DESIGN OF PILOT PLANT

7.0: The Solar Soda Works Pilot Plant has a capacity of 1000 tons Na_2CO_3 per annum. The actual production will be larger to the extent of impurities (mostly moisture) in the product. The product, will be uncalcined and sold to the Glass and Sodium Silicate Manufacturers for trial use. The users may dry the product using waste heat from their furnaces.

7.1: The design consists of

7.1.1: Area of Solar Soda Works:

Condensing and Crystallising

7.1.2: Specific. for brine pump.

7.1.3: Size of brine pipe.

Harvested material will be moved to consumers in hired trucks, from open storage at the Solar Soda Works.

7.1.1: Area of Solar Soda Works:

Based on Fractional Crystallization experiments carried out in the Laboratory (Progressive 1 and 2 and random 2), the total yield of dry material from 500 ml. of 1:4 concentrated Chitu Brine came to $8.66 + 8.80 = 24.20$ grms. (see App. 2)

The weighted average analysis of the dry solids comes to

	<u>% by wt.</u>
Na_2CO_3	92.13
NaHCO_3	2.57
NaCl	2.87

The total Na_2CO_3 incl. NaHCO_3 comes to 93.75% dry solids interms of Na_2CO_3 per 500 ml. of 1:4 conc. Chitu Brine therefore comes to:-

$$24.2 \times 0.9375 = 22.7 \text{ grms.}$$

i.e. 2 litres of original Chitu Brine yields 22.7 grms. Na_2CO_3 or 2 m^3 yields 22.7 kg. quantity of Chitu Brine required per 100 tons Na_2CO_3 comes to

$$\frac{2000 \times 1000}{22.7} = 88106 \text{ m}^3$$

7.1.1.1: The soil analysis made by Material Research and Testing Department, Faculty of Technology, Addis Ababa University shows that the soil where Solar ponds are to be constructed has the following characteristics:

Liquid Limit	85%
Plastic Limit	37%
Plasticity Index	48%
Free Swell	20%

Sieve analysis show particle size mostly between 0.1 and 0.001 mm (10% below 0.001 mm) these characteristics show the soil to be good and if the pan bottoms are rolled (by road roller when wet), the percolation losses will be reasonably low; low permeability of the soil is also indicated by absence of Alkalinity in the moist mud removed for examination from 2.75 m. below the ground surface near Chitu Meteorological Station. Taking a loss of 10% in terms of original brine, pumped volume of brine comes to approx.

$$97,000 \text{ m}^3 \text{ per } 1000 \text{ tons } \text{Na}_2\text{CO}_3.$$

7.1.1.2: Amount of water to be evaporated: This is calculated from random 2 experiment (Appendix 2).

1. Wt. of original 1:4 conc.
Chitu Brine (250 ml.): 282.2 grms.
(Sp. Cr. 1.12883)
2. Wt. of wet solids grms 17.24
3. Wt. of "Bitterns" " 107.09
124.33
4. Wt. of water evaporated 157.8 grms. This is for
8.80 grms dry solids containing. 93.73% Na_2CO_3
(total Alkali expressed as Na_2CO_3) or 8.25 grms.
 Na_2CO_3 .

Water to be evaporated per 1000 tons Sodium Carbonate comes to:-

$$\frac{1000 \times 157.8}{8.25} = 19127 \text{ m}^3$$

To this we have to add water evaporated in concentrating Chitu Brine from 4 vol. to 1 vol. This is 700 grms. approx. for 8.50 grms solid or 8.25 grms Na_2CO_3 or

$$\frac{1000 \times 700}{8.25} = 84,850 \text{ m}^3$$

Total water to be evaporated. 103,977 m^3 . This is total incl. of crystallising area. 22° Be brine, nearly saturated, will contain approx. 95 gpl Na_2CO_3 , 35 gpl NaHCO_3 , 49 gpl NaCl , 1 gpl NaF and 990 gpl H_2O . Water to be evaporated per 1000 tons Na_2CO_3 comes to 10,400 m^3 .

The quantity is larger than the brine pumped because we have taken only random 2 results for the calculations and

Random 2 yields have been lower than average of progressive 1,2 and random 2. In any case, the larger evap. will give safety margin.

- 7.1.1.3: From the Meteorological data (section 4) and water to be evaporated, we can calculate the area required. Re-examining the monthly evaporation data (Table 4.3) and rainfall (Table 4.1), the working season is 7 months i.e. from beginning of October to end of April. Even at the end of April, the brine in the condensing area can be saved and stored in a reservoir, for the next dry season. The rain which falls on the stored concentrated brine floats on the surface and can be siphoned off, with only a little dilution of the reservoir brine. Rainfall during September is less than evaporation in that month and this dilution water gets evaporated.
- 7.1.1.4: The evaporation during 210 days of dry season comes to 1632.6 mm (see Table 4.3). This is evaporation of water. In Salt Works practice, a factor of 0.8 is taken for condensing area and a factor of 0.7 for crystallising area. This is for Sea Salt Works with Magnesium Chloride in the brine. The vapour pressure of Sodium Carbonate solutions is higher and factors of 0.9 and 0.8 can be taken for the condensing and crystallising area in Solar Soda Works.
- 7.1.1.5: Area Requirements:
Water to be evap. in condensing area $103,977-10,400 = 93,577 \text{ m}^3/\text{year}$. Evaporation in working season: 1,6326m.
Area required: 6.37 Hectares (condensing area).

Area required for crystallising pans:

Water to be evaporated: $10,400 \text{ m}^3$

Area required: $\frac{10,400}{0.8 \times 1.6326} = 7963 \text{ sq. m.}$
 $= 0.8 \text{ Hectares}$

7.1.1.6: Size of reservoir will depend upon the storage necessary for the off-season. The average depth of brine in the condensing area is about 30 cm. The total brine in the condensing area at the end of the season will be $19,110 \text{ m}^3$. If we store the more conc. brine from about half the condensing area, the quantity to be stored will be $10,000 \text{ m}^3$ approx. depth of brine in the reservoir may be kept at 70 cm.

Area of reservoir:

$\frac{10,000}{0.7 \times 10,000} = 1.4 \text{ Hectares.}$

7.1.1.7: Operation of the reservoir: The level of the bottom of the reservoir is 50 cm. below the bottom level of the nearest condensing area. In beginning of March, the reservoir is short-circuited to a large extent, and allowed to go down in level. At the end of the Solar evaporation season, it is filled up to the depth of 70 cm. Partly by gravity and partly by a portable pump. Again, at the beginning of the evaporation season, the supernatant rain water is decanted, and the crystallising area is fed partly by gravity and later by pump, from the reservoir.

7.1.1.8: Layout of the Solar Soda Works: In a large Solar Works, and where the ground is fairly level, the size of a crystalliser is about 0.8 hectares. As our total crystallising area is 0.8 hectare, we may provide 2 crystallisers (in order to study and possible recovery of Baker's Soda, in the first part of first crystalliser). So each crystalliser will be 0.4 hectare in area, condensing pans in a large Solar Works are very large in area for each individual condenser, but in order to avoid short circuiting of high and low density brine, enough number will be provided. The cost of increasing the number of condensers is small as the partition walls are small. The layout will be somewhat as given in Fig. 7-1; on this layout the earthwork involved is also calculated.

	<u>m. cubes</u>
outer walls	11,530
inner walls	<u>2,720</u>
Total ...	<u>14,250</u>

The earthwork involved in digging the reservoir comes to $14,000 \times \frac{50}{100} = 7000 \text{ m}^3$ but this earth will be used for the bunds; without theodolite survey work, it is not known how much earth will be available from levelling work of the Solar evaporation area. With terracing and proper selection of the starting point for Solar Works the levelling can be reduced and it is possible that the earth dug out for reservoir and levelling, can be balanced against the above figure, and that there is a surplus earth.

7.1.2: Specifications for Brine Pump: The total quantity of brine required per annum comes to $97,000 \text{ m}^3$, the pump working hours could be taken at 20 hours during initial filling (to achieve rapid filling of the system) and then reduced to 10-12 hours per day (2 shift work and cleaning and maintenance of the engine). Excluding the reservoir, the volume of brine held in the condensing area comes to $20,000 \text{ m}^3$ or about 26% of the annual requirements of brine. A pump with a capacity of 50 m^3 per hour, working 20 hours per day, would fill up the system to working depth of 30 cm in 20 days (or to a depth of 15 cm to take advantage of large evaporation from full surface). Taking 200 working days in the season, the pump will have to work less than 10 hours a day on an average, for moistening the evaporation needs. This will then be the capacity of the main pump. Its head will be calculated after pipe size is selected in the next section.

7.1.2.1: As regards the auxiliary pump for making use of the reservoir the quantity to be handled is approx. $1/5$ of the dilute brine. A capacity of 10 m^3 per hour should suffice.

7.1.2.2: As regard the static head for the main brine pump. the max. static head required to go over the pump is 47 m. The other static head will be the difference in the level of brine in Lake Chitu and the delivery of the pipe; this will be known only after the survey, of the site and knowing the Lake Chitu surface level. In any case, by general observation, it seems to be of the order of 2 or 3 meters or even less.

Once the pump starts working, a siphon will be established and the working head will come down by 47 meters. This would affect the working of the pump and at times may create problems like cavitation and fast wearing out of impeller. The matter can be taken care of by any of the following three expedients:

- (i) Provide a priming tank at the top of the escarpment , to fill the delivery pipe.
- (ii) Provide a hand-pump (the so called donkey-pump) to fill the delivery pipe.
- (iii) Provide 2 speed arrangement for the pump to take care of the higher head at start, revert to lower speed once the Siphon is established.

In any case, we shall take the static head of the pump at 5m, total (incl. of minor entry & exit loses, dynamic head etc.) and add pipe friction loss for getting the total head loss from all causes.

7.1.3

Size of the brine delivery pipe: Pipe size is normally a matter of economics. Smaller the pipe size, larger is the frictional loss and pumping cost, but lower is the first cost. For every short delivery pipe, it is often the practice, to increase the size of the pipe by one size larger than pump delivery. In pipes of 8-10 cm and larger sizes, the velocity is usually in the range 1.5-1.7 m/sec. As we have a medium length of pipe (about 600 m). We have taken 3 sizes of pipe to choose from:

Capacity 50 m³/hr.

Pipe size mm	Velocity m/sec.	Head loss in m. per 100 m. of pipe length.
100	1.77	6
125	1.13	2
150	0.786	0.82

The total length of the pipe will depend upon the survey and the exact location of the Solar Soda Works. But, taking the nearest point when the escarpment levels out, the pipe length has been estimated by NCC officers to be 600 m. Taking another 50 m for safety and as equivalent to fittings (bends, valves, etc.) the total pressure drop works out to:

Pipe Size	Total Frictional loss meters
100	39
125	13
150	5.3

The obvious choice is 125 mm. pipe size; the total head on the pump is then 13 + 5 = 18 m, the two pumps can now be fully specified as:

Main pump	$\frac{m^3}{hr}$ 50	<u>Total head m.</u> 18
Aux. Pump	10	5

All iron construction.

- 7.2 As regards the bitterns, it is suggested that, for the pilot plant, they be dumped outside the crystallisers (with the help of the auxilliary pump or by gravity) to the ground, allowed to evaporate to dryness and collected and sold or use in preparation of detergent powders.
- 7.3 The sides of the bund walls in contact with the brine, needs protection from erosion (wave action when there is a strong breeze). This can be given either by pitching with stone or by some local material. (In Tanzanian Salt Works they use palm leaves. In India, stone pitching is quite common without use of cement of lime). Ato Dulla, who has the experience of practices in Ethiopian Salt Works could be the best judge.
- 7.4 In the crystallising area, in order to avoid lifting off some soil with the harvest, first crop of Soda product may be rolled in the pond bottom.
- 7.5 During the next visit of the Expert, a meeting may be arranged with senior staff members who have the first hand experieince of Solar Salt operations in Ethiopia. Some of the practices adopted in Solar Salt Works could be applicable to our project.



PUMP AT LAKE CHITU



ESCARPMENT

SECTION 1



PUMP DELIVERY

CONDENSER 1A

200mX110m

TOTAL SOLAR SODA WORKS
BLOCK (INCL. WALLS)

200X450m

TOTAL AREA 9 HECTARES

TOTAL OUTER PERIMETER 1300m

TOTAL RUNNING LENGTH INTERNAL WALLS
850m

OUTER PERIMETER BURG

HEIGHT 1.4m

SLOPE 1:2

ANCHOR 25cm DEEP

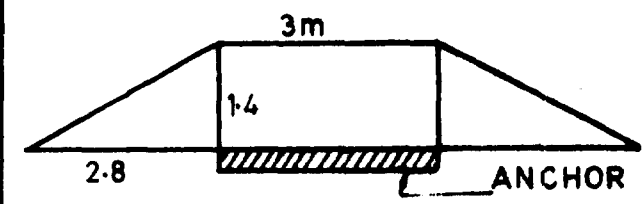
3m WIDE

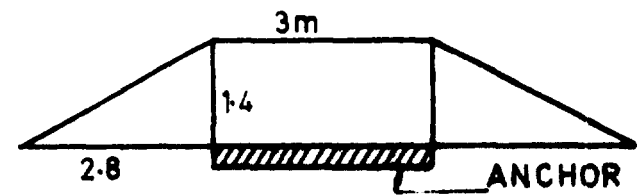
CROSS SECTION

CONDENSER 1B



CONDENSER 1C





AREA OF CROSS SECTION:
 TOTAL BASE 8.6m
 ANCHOR AREA 0.75sqm
 MAIN WALL 4.20 "

2 SIDES $2.8 \times 1.4 = 3.92$ sq.m
 TOTAL 8.87 sqm

EARTH WORK IN PERIMETER WALL
 $8.87 \times 1300 = 11530m^3$

INNER WALLS: 1m HIGH
 SLOPE 2:1 WIDTH
 TOP 12m NO ANCHOR TO BE PROVIDED

AREA OF CROSS SECTION
 MAIN WALL : 1.2 sq.m
 2 SIDE WALLS $\frac{2.0 \text{ sq.m}}{3.2 \text{ sq.m}}$

TOTAL LENGTH 850m
 EARTH WORK 2720m³

SECTION 2

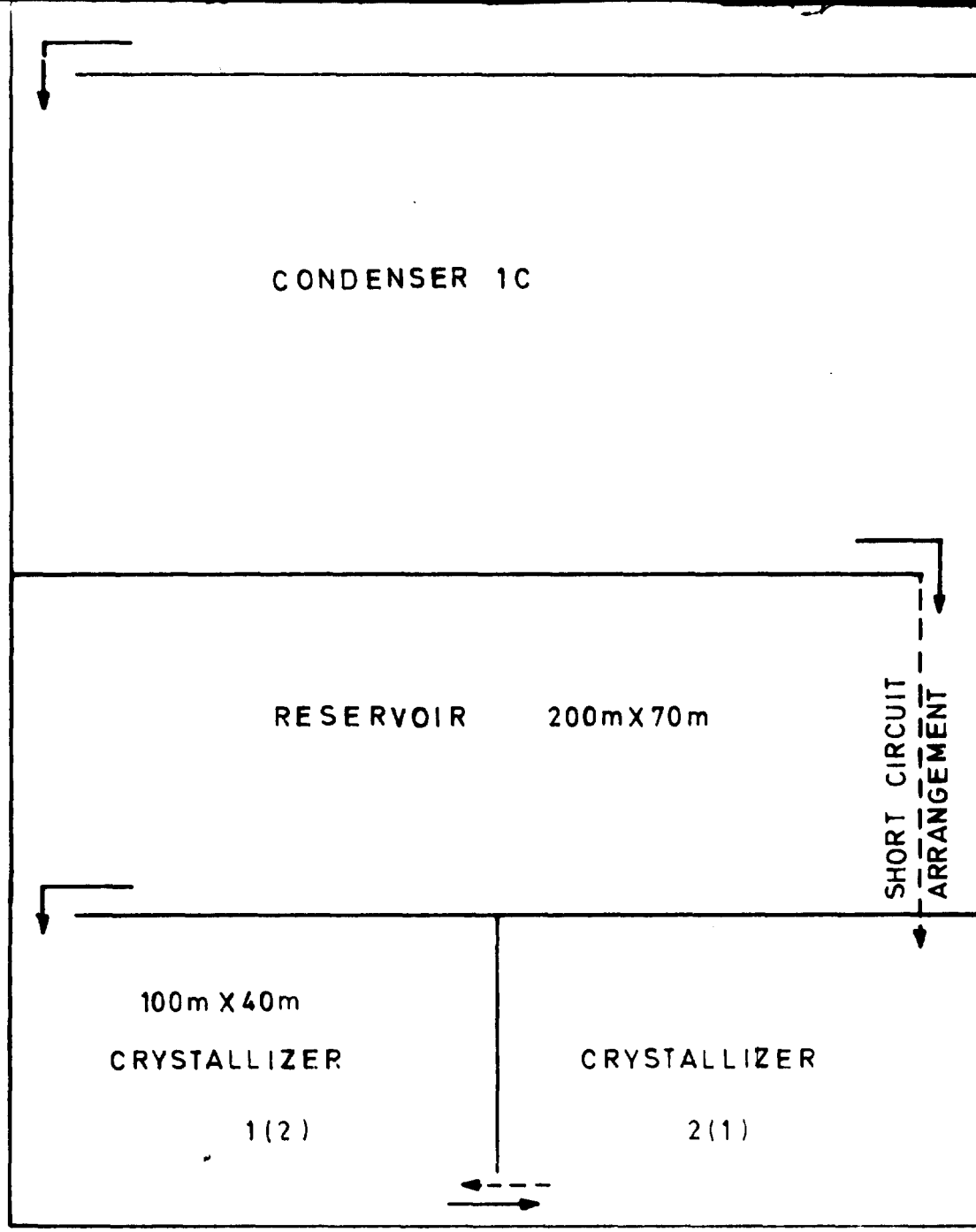


FIG. 7-1

8. PLAN OF WORK

8.0: This section deals with details of work to be carried out between now and the next visit of the Expert. It also outlines the work that the Expert will carry out during his second mission.

8.0.1: The work to be carried out by the Corporation is given hereunder:

8.1: Complete survey of the site by NCC personnel or Mapping Agency.

8.2: Preparation of the layout of the Solar Soda Works based on details worked out in section 7.

8.3: Selection and ordering the brine pump and pipe line.

8.4: Installation of pumping set, Diesel Engine, Diesel Oil storage tank, and pipe line.

8.5: Completion of earthwork, consolidation of surfaces of ponds and crystallisers.

8.6: Setting up of Meteorological Station when the instruments are received.

- 8.7: Start pumping of the brine before the consolidated pans dry-up and fill the solar evaporation ponds.
- 8.8: Laboratory work as detailed further under this heading.
- 8.9: Miscell. office work detailed later in this section.
- 8.1: The survey should start at the base of the escarpment on the northern site of Lake Chitu and continue northwards towards Lake Shalla. Total area covered should be approx. 1km. x 1km.,.
- 8.2: Based on the levels obtained in the survey Ato Dulla can prepare the layout of Solar Soda Works. It should start as near the escarpment as possible in order to save on the brine pipe, the first condensing pans can be at a slightly higher level (terracing arrangement). This will also help the flow by gravity to subsequent pans. The area to be covered is small and the layout could be simple with a relatively straight forward passage for the brine.
- 8.3: The specifications for the brine pump are detailed in the previous section. If the pump of similar characteristics is available locally, it could be purchased, in order to save time. This may involve some sacrifice of efficiency but at the diesel consumption would be quite small, this is immaterial.

- 8.4: Along with, installation of pump and accessories, install a level for the lake level. This can be attached to the suction pipe of the pump. In installation of the pump, care should be taken to keep enough free space below the lowest part of the pump, to avoid sucking up of slime from lake bottom. It is best to have axial flow type of pump which does not require a foot-value (most pump problems are connected with mal-functioning of foot-value).
- 8.5: The earthwork and other construction work should be supervised for quality, the consolidation of the bottom surface of the pans has to be done by sprinkling Lake Shalla Brine, (this is easiest to bring, if the pump is not ready) and using road roller. Once the roller work is over, the surfaces should not be allowed to be dried, if filling cannot be started for reasons of pump not being ready keep the surfaces wet by sprinkling Lake Shalla Brine. It would be best to coordinate rolling work with completion of the pump installation.
- 8.6: This work has been done once before and does not need elaboration. The site need not be softened even if it is to become a part of Solar Soda Works in future.
- 8.7: When brine pumping is started, a regular log should be maintained if start and stop of the pumping hours, diesel oil consumption pumping problems, maintenance of pump etc. general observations should also be made about percolation losses.

8.8: Laboratory work: During the first visit of the Expert. Laboratory work was carried out for a total period of about 4 weeks. Based on the results obtained/ see App. 2/ further work is required to be carried out before the next visit of the Expert. This is detailed below.

8.8.1: Arrange to get a barrel load of Chitu Brine, prepare several jerrycan hatches of 1:4 conc. brine by boiling in 1000 ml. beakers over oil-bath, allow the brine (1:4 conc.) to settle. Decant and separate the slime in the centrifuge and collect the precipitate (white). Wash 3 or 4 times with distilled water and collect. The collected precipitate should be dried at 104-106°C, ground in mortar and pestle and bottled send $\frac{1}{2}$ the sample to Central Lab. or Univ. for quantitative analysis of

Na, K, Ca, Mg,
HCO₃, CO₃, Cl, SO₄ and F.

Also, solubility in cold and hot water.

8.8.2: Ascertain Sp. Cr., CO₃, HCO₃ and Cl of 1:4 conc. Chitu Brine stock solution.

8.8.3: Take 1000 ml. of 1:4 concentrated Chitu Brine in plastic evaporating pan, and keep the same in BZT oven for fractional crystallization. The temp. should be controlled at between 28 and 30°C.

The experiments should be like the "Progressive" ones described in App. 2 when the density reaches approx. 28° Be, (plus or minus $\frac{1}{2}$ degree), filter through Buchner

filter, take the density of filtered liquor by Pyknometer, weigh the precipitate wet, dry the precipitate, at 104-106°C until const. Wt. and weigh again, filtered mother liquor should be weighed and kept for further fractional crystallization at 28-30°C until the density reaches 30° Be (1 ± half degree) collect solids on Buchner filter, weigh wet and after drying at 104-106°C Mother liquor is weighed and left for further crystallisation at 28-30°C in the B & T oven, repeat similarly for 32°Be analyse all the dried solids obtained; at 28, 30, and 32°Be. For

HCO₃
CO₃
and Cl

The results should be expressed as in App. 2 in a tabular form.

8.3.3.1: Based on the above work, the expert will carry out 2 or 3 more random experiments to determine the optimum "bitterness" density for highest yields consistent with the quality of harvested crop.

8.3.3.2: Mother-liquor obtained at 32°Be, should be weighed and analysed for CO₃ and Cl and total dissolved solids. (TDS). TDS is determined by taking a weighed sample in an evaporating dish and drying at 104-106°C to a constant weight.

8.8.4: Take 500 ml. of 1:4 conc. Chitu Brine and add 65.5 grms. dried Ca(OH)_2 , kept in a stoppered Erlenmeyer flask. (this has been analysed) boil vigorously for 30-40 min. filter through sintered glass crucible and collect the filtrate in a stock bottle. Repeat the experiment 4 to 6 times to collect large enough quantity of dilute caustic soda. (about 8-10%) analyse the liquor from stock bottle for $(\text{OH})'$, CO_3'' and Cl and density after calculating % OH, concentrate it in a glass boiler to get approx. 28% NaOH, cool, filter the separated solids (Na_2CO_3 , NaCl, Na_2SO_4 NAF etc). Through sintered glass filter and collect in another stock bottle. After completing the concentration, analyse (OH) , CO_3'' and Cl, determine the Pyknometer density and if the concentration is about 28% NaOH, use the solution for soap making and compare the soap with one obtained by using imported caustic soda.

8.8.4.1: Obtain some samples of good local lime (one currently used by sugar factory, should be one of them), hydrate with min. of water. Analyse the hydrate for Ca(OH)_2 (first end point with phenolphthalein indicator) and repeat 8.8.4 experiments with local material. Take settling test of $\text{CaCO}_3/\text{NaOH}$ slurry as was done for acetylene plant waste product and compare the setting tests. Experiment with atleast 4 or 5 samples of local lime coming from different sources of limestone quarries.

8.8.5: It is suggested that we obtain a Hydrometer of the range 0-35°Be' the one the expert has brought and left with the laboratory is of a lower range, more should be ordered for use at Chitu.

8.8.6: The following chemicals may be ordered and procured at the earliest:

- (i) Barium Chloride, Tech. Grade 200 grms.
- (ii) Sodium Carbonate A.R. Grade 100 "
- (iii) Calcium Chloride, fused, Tech. Grade 500 "
- (iv) Whatman 40 or equiv. ashless filter paper. 200 circles. of standard size (15 cm.)
- (v) Nickel Crucible 25ml. size 3 pcs.
- (vi) Sintered glass gooch crucible 25 ml. 3 pcs
- (vii) Porcelain filtering crucible 25 ml. (with holes) 3 pcs.
- (viii) Chemically pure blue asbestos acid washed 25gms.

8.8: Has been studied by Ato Abera in draft form and discussed with the Expert.

8.9: Miscellaneous office work.

8.9.1: Obtain survey drawing of Lake Chitu made by Ato Alazar, from Ministry of Industries.

8.9.2: Obtain 4 frames of aerial photograph of Lake Chitu from Mapping Agency (action already being taken by Ato Makonen).

- 8.9.3: Request Contral Lab. to check the analytical results of Lake Chitu Brine. There are some serous errors Re: balance of cations and anions. Fulor~~de~~ determination is also in doubt. Chitu Brine may also be analysed by the University.
- 8.9.4: Market survey for Soda Ash and Caustic Soda:
- 8.9.4.1: Collect import statistics - quantity^{and} and value for both chemicals for past 7 years.
- 8.9.4.2: Approach by a questionnarie, consumers of both these chemicals, and ascertain their current requirements and their estimated requirements for 1985, 1987 and 1990. Ascertain their requirements for quality also (Max. % of impunties which the process can tolerate). Determine geographical centres of consumption.
- 8.9.5: Ascertain, through Ministry of Mines (geol. survey), deposits of Gimestones and get the following details.
- A. Geogr. Location & Distance from Lake Chitu
 - B. Approx. Reserves
 - c. Chemical Analysis
Ca, Mg, SiO₂, acid insolubles CO₂ etc.
 - D. Geological Description of Type.
 - E. Collect Samples in Our Office For Physical Examination.

9. TIME SCHEDULE OF IMPLEMENTATION

- 9.0: Without intimate knowledge of local conditions and facilities available and financial resources available, it is difficult to estimate time required to implement the project, it is however, imperative to complete the earthwork and installation of the pumping set, by mid October in order to take advantage of the dry season, this will require a concerted effort on the part of all concerned. The total area of Solar Ponds is small and if the work is done with machines and work is arranged on a continuous 8-10 hours daily basis, the earthwork will be completed on schedule pump foundation may take the longest time (as it has to be given curing time) and the work should be planned with priority. Foundation Drawings can be prepared, only after ordering the pump and pump should be procured without delay.
- 9.0.1: The installation of PVC pipe will not present problems if hot-air welding and fitting facilities are available.
- 9.1: Approx. time schedule is indicated below:-
- 9.1.1: Arrange survey of site (theodolite) with NCC staff or Mapping Agency work to be completed by 20th August.
- 9.1.2: Based on the survey drawing, select site by 25th August. Meanwhile negotiate for hire of earthmoving machinery.
- 9.1.3: Select and procure pump by 20th August. Prepare foundation Drawing and cast the foundation by end of August. The pump installation can then be started by 3rd week of September and pump installed by beginning of October.

- 9.1.4: Earthwork can start in early September and completed by early October. Consolidation and rolling can start as the earthwork gets completed, pond by pond, and complete by mid-October.
- 9.2: Pumping of brine can start by 15th/20th October. First filling of the brine should be expedited by working the pump for 18-20 hours per day. (rest of the time for routine maintenance). In order to have the maximum evaporation, the brine should be allowed to spread over as vast an area as possible, through gravity flow. Depth in condensing area should be **built** up gradually.
- 9.3: Brine should be admitted to crystallising area after it reaches 20-21° Be' much before this, all the Ca and Mg (present in traces) will have been precipitated.
- 9.4: Once the entire system of Solar Ponds has been filled up with brine, the pumping hours should be reduced to maintain levels. (Approx. 30 cm. in condensing area and 50-60 cm. in reservoir. The level should be 15 cm in crystallising area over the layer of solids).
- 9.5: Harvesting implements should be procured, (similar to ones used in Solar Salt Works) by end of November.
- 9.6: At the stage of Pilot Project, the harvesting crop will be stored in the open and moved expeditiously to the market for trials. Handling can be in bulk or in used bags, in hired trucks.

10. EXPERTS PROGRAMME AND WORK PLAN

- 10.0: If everything goes on according to implementation programme given in section 9.0, the Expert should visit Ethiopia by mid-December. His work during the second mission, lasting approx. 3 more this will be:
- 10.1: Study the Laboratory Work done in the interim period and organise some more random crystallisation experiments.
- 10.1.1: With the results of progressive crystallisation work and random experiments, determine the parameters for Solar Soda works operation (highest "bitterns" density consistent with quality of Soda).
- 10.2: Study the meteorological data obtained in the interim and correlate with data collected earlier. (section 4 of the report).
- 10.3: Operation of Solar Soda Works and establishment of parameters (density of brine for admission to crystallisers and density of brine for discharge).
- 10.4: Collecting samples from various ponds and organising their analysis in our own (NCC) Laboratory .
- 10.5: From the quality of solids obtained in the Solar crystallising pans, to decide whether it is possible to isolate Bakers Soda as a Co-product.

- 10.6: To improve the quality of Soda by washing or recrystallisation.
- 10.7: Study actual evaporation rate in Solar Soda Works and compare it with meteorological data collect design data for full scale Solar works.
- 10.8: Study the results of market survey. This will help in deciding the size of the full-scale plant.
- 10.9: Study the investigations on lime stone deposits, study the Chemical Caustic preparation work in the Laboratory with locally available lime examine whether Chemical Caustic Soda Project is worth pursuing further.
- 10.10: Prepare questionnaire for collecting data for an economic evaluation in the final visit of the Expert.
- 10.11: Train personnel in operation and maintenance of the pilot plant.
- 10.12: Train personnel in the analytic tests in NCC Lab. at Addis Ababa

APPENDIX 1

Visit to Lake Shalla and Lake Chitu.

- 1.1 Ato Mekonnen Tessema and the UNIDO Expert left Addis Ababa on 21st June after lunch and reached Shashamene in the evening. We left for the site next day morning and spent the whole day there visiting the two lakes and several hot springs on the Southern Shore of Lake Shalla. Dry & Wet bulb. temp. reading were taken.
- 1.1.1 On the second day, we visited the southern shore of Lake Chitu, as also some hot springs. Only the southern shore of Lake Chitu has some open land but the area is not enough to develop any solar evaporation works. We collected a barrel of the Lake Brine for evaporation experiments in open pan. A small observatory was set up at the forest conservatory Bungalow to take the following readings:
- a) Dry and wet bilb. temp.
 - b) Anemometer Readings
 - c) Fresh water evap.
 - d) Chitu Brine evap.
 - e) Rain-gauge.
- 1.1.2 On 24, 25 and 27th June, we continued to take observatory readings and inspection of site. We also collected soil samples from three points on the site between the two Lakes. General examination showed the soil to be very fine in particle size and free from grit. Wetted soil was good in plasticity. A slurry of soil in water showed

extremely poor setting, again confirming fine particle size. A pit dig for soil sample, when filled up by a barrel of Lake Shalla Brine, showed rapid to moderate percolation, indicating need for consolidation during solar evaporation pan construction.

1.1.3 On 28th June, we visited hot spring no. 30 on the eastern shore of Lake Shalla. This spring can be reached easily by driving north from Shashamene for 37 km. on the asphalt road to Addis Ababa and then turn left on a paved road. There is a sign board marked "Lake Shalla". About 6 km. on this road, we see Lake Shalla and a walk of about 200 m. brings us to the boiling water springs. Water temp. was measured to be 94 and 95°C in two different locations. Due to alluvial nature of the soil, the springs have eroded the earth in several places and we saw gaping holes made recently (in the last 10 years or so according to the forest conservatory men). The boiling point of water at the altitude (about 1570 meters) would be 95-96°C and in one of the large pits, water was bubbling. The total quantity of boiling water springs has been recorded as 33.3 litres per second. The spring water has been analysed earlier and it was calculated that this single spring adds 3,100 tons of Soda Ash (Na_2CO_3) to Lake Shalla. Both in temperature and volume, this is the most important and largest spring near the Lake Shore.

1.1.4 After visiting the boiling water springs, we proceeded further north on the Addis Ababa Road. The forest conservatory office is 42 km. from Shashamene. 19 km further north on the main Asphalt Road, we turned right.

About 12 km on the track, we came to the Base Camp of the Geothermal Project. (U.N.D.T.C.D. Project ETH/78/007). From the Base Camp, the drilling site is 26 km. away on mountainous but smooth track. At the drilling site, we met Mr. Roy Johnstone, in charge of drilling operations. Drilling of one well has been completed (to over 2100 m) and the drilling rig had been shifted to another site about 1 km. away. Drilling on this site has to start early in July and would take about 3 months. The first well which was completed would be opened up in about a months time and then they would know about the permeability of the rock structure and the quantum of energy available. About the permeability, indications obtained during drilling operations and water injection, indicate poor permeability though it can improve somewhat after the well is opened. The indications about the quantity of steam are in the order of 15 kg. per second. (54 tons per hour). Temperature upto 300°C are expected. (for calcination of Soda Ash, we need steam temperature of 225-228°C and a quantity of 5 tons per hour for a production of 20,000 tons per annum). This will correspond to a medium to small size power plant, The cost of the drilling rig is about US\$6 million. Each well drilling costs about \$ 1.5-2.0 million and investigation of a field takes \$ 10-15 to determine whether it is worth putting up the power plant. Wells which are too small to exploit for power generation could be used for steam re-uses for Soda Ash calcination and Caustic solution evaporation.

According to Mr. Roy Johnstone, even after a geothermal field is commissioned, it is difficult to say how long it will last. 30 years life is considered to be good. The geothermal station in New Zealand is already 30 years in operation and even now, it is not known how long it will continue.

The permeability of the rock is the most important factor. It is judged from the examination of the rock obtained as core during drilling and by enjecting fresh water (from Lake Zwai) and seeing the pressure rise and temperature rise. Water was injected at about 18000 lts. per hour. This water would penetrate in the direction opposite to the ultimate flow of steam. This two directional flow (of water and steam) would also improve the permeability of the rock.

1.1.5 In Mr, Roy Johnstone's opinion, Lake Langano site is a little too far from Lake Chitu (nearly 140-150 km). The best site for our project (SI/ETH/81/803) is Corbetti Caldera, hardly 20/25 km south of Lake Chitu. This site has very favourable indications of geothermal activity (large number of fumaroles). In fact, in the project (U.N.D.T.C.D. ETH/78/007) it was originally planned to include Corbetti Caldera for full field investigations. It is however, now given up and they will fully concentrate on Lake Langano site.

1.1.6 We returned to Shashamene over another route via Adami-tulu. This route to south is longer than the route by which we came to the Lake Langano drilling site but is shorter in 2 respects: vis. it takes us to the asphalt

highway in shorter distance (15-20 km) and it is a shorter route to Addis Ababa. (About 165 km). The road from drilling site to the main road, however, is rough in places and there is a Bailey Bridge over river Bulbula.

- 1.1.7 On 29th June, we dug a pit inside the evaporation pan constructed earlier (south of the meteorological station). Digging upto 2.5-2.6m depth produced only wet sticky thick mud and further digging was difficult. The wet mass was suspended in fresh water (PH 6.8-7.0) and PH measured again. There was little change in PH indicating the absence of alkaline brine in the interstitial part of the soil. The local people said even digging a pit very near the lake shore at Shalla produced some liquid only 4 m. below surface. This experiment showed that it is difficult to get sub-soil brine, and that Chitu Brine will have to be pumped over the 47 m. high escarpment. The experiment, however, indicates the favourable nature of the soil (low permeability) for construction of Solar evaporation ponds.

A sample of the sticky thick soil from 2.6 m. below surface, has been brought to Addis Ababa for general inspection.

- 1.1.8 We continued the observatory readings until 30th and returned to Addis Ababa on 1st July. The important readings are summarised below in Table 1-1 and Table 1-2.

Table 1-1
Evaporation: Vertical mm, Water & Chitu Brine

Date	Fresh Water		Chitu Brine		Remarks
	mm	Duration hrs.	6° TW (1.03 Sp.Gr)		
			mm	Duration	
23	6	7 (Day Time)			
23-24		16½ (Over night)	-	-	Chitu Brine in Big Pan 120 cm. Ø, 155.3mm deep 175.6 ltr. taken at 12- 30 hrs.
24	7	7 (Day Time)	4.3	16	Bird guard provided over fresh water Bowl.
24-25	4	16½ (Over night)	3	16½ hrs	
25	6	6½ hrs (Day time)	3	6½ hrs	
25-27	14.2	41½ hrs	12	41½ hrs	Rainfall 3.2 mm. Big pan covered. Fresh water evap. corrected for wind wind 10 km/hr.
27-29	11	48 hrs.	6	48 hrs.	Big pan covered 24 hrs. Density Chitu Brine 7.1 TW (1.0355) Rain 0.23 mm.
29-30	2	17¼ hrs.	2.5	24 hrs.	Cloudy wind 3 km/hr.
30	2.45	4½ hrs.	0.3	4½ hrs.	Big pan covered most of time. Wind 3 km/hr.

1.1.9 The existing rain-gauge has been calibrated so that we can make use of it by measuring the volume of rain water collected. The area of collecting funnel is 200 mm. Based on this, 1 mm. of rain corresponds to a collection of 31.42 ml. of water. Table 1.3 gives the relationship collection of water to mm. of rain and vice versa.

Table 1-3
Rain Gauge calibration

Ml. Water Collected	Rain-fall mm.	Rain-fall mm.	Water Collected ml.
5	0.159	1	31.42
10	0.318	2	62.83
15	0.477	3	94.25
20	0.637	4	125.66
25	0.796	5	157.08
30	0.955	6	188.50
35	1.11	7	219.91
40	1.27	8	251.33
45	1.43	9	282.74
50	1.59	10	314.16
60	1.91	12	377.0
70	2.23	14	439.8
80	2.55	16	502.7
90	2.86	18	565.5
100	3.18	20	628.3
200	6.37	25	785.4
300	9.55	30	942.5
400	12.73	35	1100
500	15.92	40	1257
1000	31.83	45	1414
		50	1571

Table 1-2
Dry & Wet Bulb Temperature

Date June '83	Time hrs	Dry Bulb °C	Wet Bulb ° C	Difference °C	% Relative humidity
23	16-15	31.9	24.8	7.1	57.6
24	9.45	22.4	20.0	2.4	81.3
	11.30	26.4	21.0	5.4	63.3
	14.00	29.2	23.3	5.9	62.2
	15.15	28.2	22.4	5.8	62.2
	16.45	27.3	20.1	7.2	53.5
25	9.00,	22.2	18.4	3.8	71.0
	11.00	24.5	19.4	5.1	63.8
	15.00	29.2	19.4	9.8	41.8
27	9.00	20.8	18.0	2.8	77.5
	11.45	26.00	19.6	6.4	57.0
	14.40	23.00	17.4	5.6	59.4
29	9.10	24.4	19.2	5.2	63.1
	11.40	30.6	22.0	8.6	49.0
	15.45	22.0	18.1	3.9	20.1
30	9.30	23	19.2	3.8	71.5
	14.00	29	22.8	6.2	60.4

APPENDIX 2

Laboratory Work

2.1 Considerable Laboratory work was carried out on Chitu Brine. The work was divided into 3 sections.

2.1.1 Chemical analysis and physical properties

2.1.2 Fractional Crystallization

2.1.3 Preparation of Chemical Caustic Soda.

2.1.1 Chitu Brine was analysed for HCO_3^- , CO_3^{2-} and Cl. The methods of analysis are described in Appendix 3. The analysis of Chitu Brine as carried out by us is given in Table 2.1 along with the recent analysis carried out by Central Laboratory and the earlier analysis reproduced in Mr. Du Bois' Reports.

Table 2-1
Chemical Analysis of Chitu Brine
Major Constituents in gpl.

	Our Analysis	Central Lab.	Du Bois' Reports
HCO_3^-	3.296	1.650	5.112
CO_3^{2-}	13.839	12.400	10.758
Cl	5.964	7.285	5.900

The discrepancies in CO_3 and HCO_3 concentration in the three sets of analysis are probably due to the tricky nature of the method of determining of HCO_3 and CO_3 when they co-exist, (see Appendix 3). As regards the high Cl contents in the results of analysis of central

laboratory, it should be noted that there is some serious error in the Central Laboratory results of analysis of Chitu Brine as the total cations add up to 1505.38 molal equivalents whereas the anions add up only to 665.19 equivalents.

2.1.2 During progressive concentration of Chitu Brine before separation of any salts, Sp. Gr. of solutions were determined. The results are tabulated below: TDS were calculated from original TDS values and volume reduction.

Table 2-2

Sp Gr. of Chitu Brine with progressive evaporation

<u>TDS</u> <u>gpl</u>	<u>Sp. Gr.</u> <u>at 20/21°C</u>
37.34	1.0304 (original Brine)
50.50	1.0420
73.82	1.0623
125.78	1.1066
148.47	1.12125
201.40	1.1673

2.1.3 The total dissolved solids in Chitu Brine were determined directly by one step evaporation of a weighted sample and drying the solids at 120°C to constant weight, 800 ml. of chitu Brine gave 29.87 gms of dried solids giving 3.734 gms per 100 ml. or 37.34 gms per litre. The probable composition of Chitu Brine, calculated from anion concentrations is given below.

Table 2-3
Probable Composition of Chitu Brine

Component	Gpl	Remarks
Na ₂ CO ₃	24,449	Analysis in our lab.
NaHCO ₃	4,539	" " " "
NaCl	9,878	" " " "
Na ₂ SO ₄	0.59	" quoted by Du Bois
NaF	0.20	" " " "
	39.656	

The direct determination of TDS is lower than the probable composition because during progressive drying of solids even at 120°C most of the Bi-carbonate gets converted to Sodium Carbonate. This happens even during Solar evaporation of brines at lower temperatures. If we take all HCO₃ as equivalent CO₃, the calculated TDS comes to 37,98 gpl which shows a good agreement with the one directly determined.

2.1.4 According to Table 2-3 the total dried solids after calcination to Na₂CO₃ should have 27.313 gms Na₂CO₃ in a total dried solids of 37.98 gms or by % 71.9%.

The dried solids, after calcination, analysed 71.01 Na₂CO₃. The agreement is close and confirms that the CO₃/HCO₃ determinations made by us in our Laboratory are reliable.

2.1.5 Sp. Gr. Vs TDS (Table 2-2) results have been plotted and presented in graph Fig 2.1.

2.1.6 During progressive evaporation of Chitu Brine, the boiling points were taken at a few points. The results are tabulated below:

Table 2-4
Boiling points of Chitu Brine at
various concentrations

TDS gpl	Boiling Point °C	Remarks
0	93°	Distilled Water
37.34	93.5	Chitu Brine
47.87	94.	
103.2	95.5	
149.4	96	

During final stages of evaporation to a concentration of 1 to 4 (149.4 gpl TDS), there was some foaming, probably due to organic impurities and evolution of carbon dioxide gas (decomposition of HCO_3 ion).

2.2 From the general considerations of solubility data given in J.E. Teeples Book on ~~sezries~~ Lake Brine and the composition of Chitu Brine it was felt that precipitation of Na_2SO_4 and NaF would occur at a stage later than precipitation of NaCl . In any fractional crystallization, therefore, if we control the precipitation of NaCl , the precipitation of NaF and Na_2SO_4 will automatically be controlled.

In all the fractional crystallization experiments, we started with a brine stock concentrated from 4000 ml to 1000 ml by boiling of Chitu Brine. This concentrated brine was evaporated in porcelian dish at a constant temperature of 39-40°C in a heating oven with thermo-static control. The evaporated mass was filtered through a Buchner funnel and the brine obtained by filtration was analysed for CO₃, HCO₃ and chloride and its Sp. Gr. was determined. The solids were dried at 105°C and weighed and analysed for HCO₃, CO₃ and chloride. In case of a final sample, the solids obtained by fractional crystallization of 250 ml conc. Chitu Brine were washed with 10 ml of Conc. Chitu Brine followed by washing with 5 ml of Chitu Brine. One of the samples was fractionally crystallized in two stages, separating the solids in two steps, and using brine obtained from first stage to yield a second conc. the results of fractional crystallization are presented in Table 2-5 below.

Table 2-5
Fractional Crystallization of 250 ml of
1:4 Conc. Chitu Brine at 39-40°C

Sample Description	Brine				Solids					
	Weight	Sp.Gr.	gpl		Weight		H ₂ O	% by Weight		
			CO ₃	Cl	Wet	Dry		NaHCO ₃	Na ₂ CO ₃	NaCl
Progressive 1	gms	1.1133	-	-	13.44	8.66	35.6	2.83	92.86	2.20
Progressive 2	-	1.2954	123.5	-	9.43	6.74	28.5	-	92.63	6.84
Random 1	25.11	1.3187	151.5	85.52	17.64	10.49	40.5	4.01	89.62	5.16
Random 2	107.09	1.278	128.4	73.85						
Solids washed with Brine					17.24	8.80	49.0	4.29	91.02	2.78

Note: 20. gr. of progressive 2 Brine is an unfiltered sample with some suspended solids.

2.2.1 The moisture content in the crystallized solids filtered on the Buchner varied considerably due partly to density of the brine but mainly due to vacuum obtained by the water pump which would depend upon the water pressure. This variation could also be due to formation of $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ in part. The sodium chloride content, would be a function of density of brine from which solids are filtered off.

2.2.2 During the experiments with 1:4 concentrated Chitu Brine, it was observed that the concentrated brine which was fairly clear when hot, appeared cloudy on cooling, on centrifuging we got white precipitate. The precipitate, even after washing with distilled water, indicated presence of some alkali on filtration with $\frac{N}{10}$ hydrochloric acid. The precipitate, however, was mostly insoluble in strong hydrochloric acid and mostly soluble in hot water. The precipitate could be some complex double salt., insoluble in cold water but is decomposed into its constituents by hot water. Dr. Berhanu has suggested that we collect some quantity of this precipitate and send half the quantity to the Central Laboratory for complete analysis.

2.2.3 Preparation of Chemical Caustic Soda: As Chemical Caustic Soda can be made profitably from concentrated Chitu brine, the cost of production of which would only be a fraction of solid saleable Soda ash, some experiments were conducted in the Laboratory using 1:4 concentrated Chitu Brine.

Waste lime slurry was obtained from the Acetylene plant as source of lime. The quantity of lime available from the acetylene plant was subsequently found to be too small to have any economic significance (The total quantity available in Addis Ababa plant can make only about 80 tons caustic soda per annum). After analysing the lime slurry (For method of analysis see Appendix 3) adequate quantity of slurry was added to 1:4 concentrated Chitu brine (29 gas wet slurry per 100 ml Chitu)(Conc. brine), and the solution boiled for 30-40 minutes. A settling test was taken on the hot solution with the following results.

Table 2-6 settling test
Chemical Caustic Slurry

Time min.	% Clear liquor
5	14
10	25
15	35
20	43
30	58
40	63
50	62
70	62

In all, 2 experiments were conducted and the results were summarized in the following table.

Table 2-7

Preparation of Chemical caustic soda, using Acetylene Plant lime slurry (10% over theoretical requirements).
Time of reaction 30-40 minutes. Temp. 97-98°C.

S. No.	Conc. Chitu Brine ml.	Liquor Analysis			% Conversion
		% NaOH	Na ₂ CO ₃	NaCl	
1	150	6.77	2.26	4.27	80
2	500	6.91	1.67	4.19	84.5

Material Balance was taken and it was found that of the input of 16.57 gms of Na₂CO₃ in Chitu Brine, 11.73 gms was accounted for in concentrated NaOH solution, 4.79 gms in washings (of CaCO₃ mud) and 0.05 gms unaccounted. In the regular plant practice, the washings as also unconverted Na₂CO₃ would remain in the system.

2.2.4 A large quantity of dry (Ca(OH)₂) has been prepared by drying the slurry at 105°C. This was fground and stored in a rubber stoppered container, This dry hydrate analysis 65.3% Ca(OH)₂.

For future use, and preparation of Chemical Caustic Soda, use for every 100 ml 1:4 concentrated Chitu Brine.

13.1 gms dry hydrate

This will provide 10% excess over theoretical.

APPENDIX 3

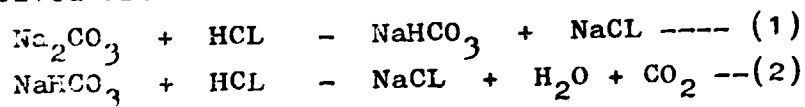
Methods of Chemical Analysis: Chitu Brine and related Products:

3.1 The existing facilities and Chemicals available make it possible to analyse Chitu Brine and other related products to the following analyses:

- 3.1.1 Determination of HCO_3^- and CO_3^{2-}
- 3.1.2: Determination of Cl^-
- 3.1.3: Available CaO or $\text{Ca}(\text{OH})_2$ in lime or slurry of $\text{Ca}(\text{OH})_2$.
- 3.1.4: $(\text{OH})^-$ and CO_3^{2-} in Chemical Caustic Soda.

These methods are described below:

3.1.1 The determination of bicarbonate in presence of Carbonate is tricky and involves some skill. The chemical reactions involved are:



Titration with decinormal hydro chloric acid using phenolphthalein as indicator corresponds to reaction (1) above, further titration, using methyl orange as indicator is represented by reaction (2). During the first part of the titration using phenolphthalein as an indicator, care has to be taken that the second part of reaction does not take place at all. If CO_2 gets released it is irreversible reaction, and will indicate high results for Na_2CO_3 and low results for NaHCO_3 . The first titration is therefore carried out with the following precautions:

- A. Chilling the solution to about 5°C
- B. Addition of HCl solution very slowly (drop by drop throughout the titration) and
- C. Keeping the burette under the solution and all the time, vigorously stirring the solution, to avoid excess acid in any part of solution.

Only by observing the above precautions, bicarbonate can be determined accurately.

Calculations: According to reaction (1), Phenolphthalein (P) titration, indicated $\frac{1}{2}$ the Na_2CO_3 . So, 2p indicates Na_2CO_3 . Total reading (M.O.) indicates $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$. So M. O. minus 2p indicates bicarbonate. Example :
1:4 conc. Chitu Brine: 1.10975 grms conc. Brine (eq. to 0.9831 ml) titrated against decinormal (0.1039 N) HCl. Required 9.1 ml with phenolphthalein indicator and 19.75 ml. total M.O. reading (in Cl, P). m-2p corresponds to NaHCO_3 (1.55) and 2p corresponds to Na_2CO_3 (18.2) gpl NaHCO_3 is then:-

$$\frac{0.1039 \times 1.55 \times 84}{0.9831} = 13.76$$

gpl Na_2CO_3

$$= \frac{0.1039 \times 18.2 \times 53}{0.9831} = 101.94$$

Similarly, it can be calculated for solid products.

3.1.2: Chloride determination: The method used is Mohr's method of direct titration with decinormal solution of silver nitrate, using 5% solution of Potassium Chromate as indicator. The procedure for Alkaline solutions is: Take a little portion of the solution, add 3 drops of methyl orange indicator, neutralise dropwise with dilute nitric acid (free from Chloride) add a pinch of pure Sodium Bicarbonate (free from Chloride) and add 3 drops of Potassium Chromate indicator. Titrate against N/10 AgNO_3 Solution. Collect precipitate of AgCl for recovery of Ag. (In the collected AgCl precipitate in an evaporating crucible, add a piece of flat iron and 3 drops of HCl (strong) and some water. AgCl will get converted into black metallic silver and equivalent Fe from iron piece will go into solution as FeCl_3 , wash the precipitate with distilled water until free from Cl and dissolve in strong nitric acid. This silver nitrate solution can be used again after standardisation).

Calculations of Cl' : Example:

5 ml Chemical Caustic Solution made up to 100 ml.

5 ml of this solution from volumetric flask required.

2 ml of 0.1 N AgNO_3

$$\text{gpl NaCl} = \frac{2}{5} \times 0.1 \times 58.5 \times \frac{100}{5} = 46.8$$

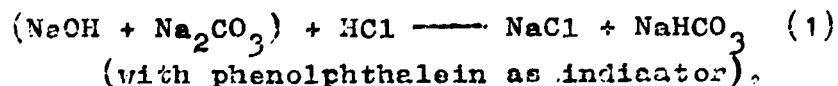
Similarly, determination of Chloride can be carried out in solids, taking known weight, making to known volume and taking a little portion for analysis.

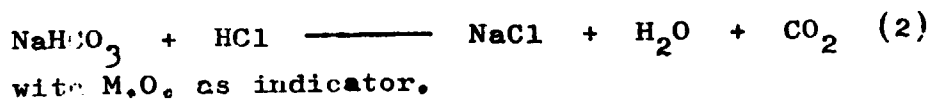
3.1.3: Available CaO: In commercial lime, CaO occurs in two forms: Available CaO which hydrates easily to form active $\text{Ca}(\text{OH})_2$ and some CaO which is inactive in the form of dead-burnt CaO or as Silicates. This is not available for most reactions requiring $\text{Ca}(\text{OH})_2$. The method described below is approximate but quick and is used by the Alkali Industry. The method consists of titration of the hydrated sample mixed in water, with standard Hydrochloric Acid, using phenolphthalein as indicator, and taking the first end point. The titration should be carried out fast, (dropwise but several drops per second). After the end point is reached, the red colour appears again, as some slow-reacting CaO attacks the acid but this is neglected.

Calculations: Example: 0.10138 gms. dried $\text{Ca}(\text{OH})_2$, diluted with distilled water required 17.1 ml. 0.1039 N HCl for the first end-point.

$$\% \text{Ca}(\text{OH})_2 = \frac{17.1 \times 0.1039 \times 37 \times 100}{100 \times 0.10138} = 54.52\%$$

3.1.4: $(\text{OH})^-$ and CO_3^{2-} in Chemical Caustic Solutions:
When Sodium Carbonate is reacted with lime slurry, some Carbonate always remains unreacted and chemical analysis is necessary to determine the unreacted CO_3^{2-} . The reactions during titration are as follows:





If we take M.O. reading as the total (m-p) x 2 is the total Na_2CO_3 and 2p-m is the NaOH

Calculations, Example:

5 ml. Chemical Caustic Liquor made up to 100 ml, 10 ml. of this diluted solution required 10.15 ml. 0.1039 N HCl with Phenolphthalein indicator and a total of 11.00 ml. with M.O. indicator.

$\frac{1}{2}$ Na_2CO_3 needed 0.85 ml.
 Na_2CO_3 ===== 1.70 ml.
NaOH ===== 9.30 ml.

NaOH gpl in original liquor =

$$= \frac{9.30}{10} \times 0.1039 \times 40 \times \frac{100}{5} = 77.30$$

$$\text{Na}_2\text{CO}_3 \text{ gpl} = \frac{1.70}{10} \times 0.1039 \times 53 \times \frac{100}{5} = 18.72$$

3.2: A document giving various methods of analysis of F⁻ has been handed over to Ato Asrat. Due to low fluoride contents of Chitu Brine, it will not be necessary to carry out fluoride determination as a routine analysis. Occasionally, it could be got done outside (Central Laboratory). Sulphate determination can be done only after we have a muffle furnace for ignition. This determination also could be got done outside, until we have the muffle furnace.

3.3: Analysis of Cations is unnecessary for routine quality control.

The above covers all the major constituents of Chitu Brine.

Appendix 4. Comparison of Alkali Reserves in Lake Shalla, Lake Chitu, Lake Magalli and Lake Natron

Particulars	Lake Shalla	Lake Chitu	Lake Magalli (Kenya)	Lake Natron (Tanzania)
Latitude	7° - 25'N	7° - 22'N	1° - 50'S	2° - 20'S
Longitude	38° - 30'E	38° - 34'E	36° - 16'E	36° - 10'E
Existence of salinity	-	-	1--20x10 ³ years	
Area Sq. km	39.4	0.93(?)	75	900
Thickness of crust/ or depth of Brvne meters	Deepest 257	8.5	4 - 40 (av.20)	0.45 (average)
Lake level above m.s.l. meters	1570	?	580	610
Reserves of Na ₂ CO ₃ million tons	421	0.86	3000	135
Replenishment million tons	0.005	Negligible	1.5 (gross) 0.5 (net)	1.1 (gross)
Water input from rivers & springs million m ³ per day	-	-	85	-
Temp. of hottest springs °C	96	60	85	53
Rainfall mm	Less than 800	Less than 800	384 (average)	384 (average)

(Appendix 5)

List of important Books for Laboratory and for general
Library. to be procured.

1. Snell D. Foster: Encyclopedia of Industrial Chemical Analysis
(complete set).
John Wiley V sons Inc.
2. Cocks L.V. et al, Laboratory Handbook for oil and Fat
analysis. Academic press Inc.
3. Vogel 1. Arthur, text book of practical Organic Chemistry
the English Language Book Society; Longman.
4. Bockenoogen H,A, analysis and characterization of Oil, Fats
and Fat products Vol. I & II
John Wiley & Sons Inc.
5. Cooke 1. Edward Chemical synonyms and trade names C.R.C.
press Inc.
6. Marvin C.F, Psychrometric Tables U.S., Dept of Commerce.
Wather Bureau.
7. Smithsonian Meteorological Tables Smithsonian Inst.
Washington.
8. Sodium Chloride, the production and properties of Salt
and Brine, D.W. Kaufman. Newyork, 1960.
9. Extraction of Chemicals from Sea Water, Inland Brines and
Rock Salt Deposits. Documents 1.D/73. U.N. 1972.
10. The Industrial Development of Searles Lake Brines. J.E.
Teeple Chemical Catalogue Co. (1929)
11. Solubilities inorg. and metal org. compounds Seidell
(linke) Vol. I & II.
12. Geothermal energy Ed. Kruger and Otte Stam Ford Univ.
press 1973.
13. T.P.Hai, Manufacture of Soda Reinhold Monograph No. 65.
(1942).

14. 1. Pateu and N. Dimitriu (English Ed.) published in Romania.
15. Zoran Rant, German publication. Manufacture of Soda.
- 16-19. There are four Russian Books in Soda Ash:
 - Saas - Tissowskij (1932)
 - M.P. Sytin (1947)
 - J.R. Goldstein (1934; 1956)
 - J.J. Gessen (1951)
20. Guidelines for the establishment of Solar Salt facilities. M.G. Venketesh Mannar, UNIDO 15/330 (1982)
21. International Symposium on Salt and Marine Chemicals (1982) Central Salt and Marine Chemicals Research Institute. India.

Appendix 6: CALCULATIONS OF RELATIVE HUMIDITY FROM DRY
AND WET BULB TEMP.

During the interim period, whilst we are waiting for instruments for continuously recording the relative humidity. If we want to maintain records of this parameter the percent humidity can be calculated from the dry and wet bulb temp. using the following formula (the Expert has also included in the list of books to be acquired psychrometric tables which also gives the readings at a glance.)

$$e = e' - 0.00066B (t-t') (1 + 0.00115 t)$$

where

e = Vap, pressure of aq. vapour in air at t °C

e' = Sat. Vapour Pr. of water at t' °C

t = Dry bulb temp. °C

t' = Wet bulb temp. °C

B = Barometric Pressure in mm Hg.

Relative Humidity is found by dividing e with Sat. V.P. of water at t °C.

For our observatory sit, at Lake Chitu, B = Approx. 635mm. Hg, and the formula can be rewritten as

$$e = e' - 0.4191 (t - t') (1+0.00115t')$$

Appendix 7. IMPORTANT DISTANCES

	<u>km.</u>
1. Addis Ababa to Shashamene	250
2. Shashamene to Solar Works Site	39
Asphalt Road 23km.	
Village Track 16km.	
3. Shashamene to Boiling Water Spring	43
on east coast of Lake Shalla 37km.	
on Asphalt Road plus 6 km. truck	
4. Shashamene to Geothermal Drilling	108
site via Adama Tulu	
5. Shashamene to Geothermal Drilling site	99
via their base camp.	

