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20686

SI/CPR/92/302

19 November 1993

FINAL MISSION REPORT

ON

ASSESSMENT/ANALYSIS OF THE ALUMINA TECHNOLOGY AND RED MUD
DISPOSAL PROCESS IN GUIZHOU ALUMINA PLANT
CHINA

BY

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TECHNICAL CONSULTANTS

Backstopping officer: T. Gróf, UNIDO substantive officer

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Vienna

ABSTRACT

- Project No : SI/CPR/92/802
- Project title: To improve the environmental impact of the Guizhou Alumina Plant with special emphasis of red mud treatment and disposal, reduction of wastes
- Objective : To provide CNNC and Guizhou Alumina Plant with high level consultancy service which will assist CNNC and the National Environment Committee in evaluating different technology choice in red mud handling and processing
- Duration : 2 weeks total including 1 week field work and 1 week service at home base

Conclusions

1. The technological water balance exhibits a serious non - equilibrium state, the reasons of which are:
 - The direct steam heating system applied in the Bayer alumina production line dilutes the sodium-aluminate-solution
 - Other, not measured and known quantity of water/i.e. cleaning, centrifugal pump sealing water/may also dilute the system
2. The washing efficiency of red mud produced by both in the Bayer and Roasting production lines is very low due to the followings:
 - The components of wash water (i.e. recycled pond water, alkaline condensate water) are containing high caustic concentration ranging from 15 to 40 g $\text{Na}_2\text{O}/\text{l}$.

- The operation of red mud washing lines exhibits an irregular state/i.e. the concentration stages of the red mud washers are not showing the usual (required) values.

3. Because of point 1 and 2 above, in the red mud lakes huge amount of disposed water (approx. 1.5 million m³) has been accumulated. The caustic content of the disposed water is very high (approx. 12-15 g Na₂O/l) and has an adverse effect for both the red mud washing and the environment.

The environmental impact of this waste is harmful since the high alkaline content waste has been penetrated into the ground and contaminating the water used for agriculture/industry and drinking water. The level of contamination reaches the pH9 level even 1 to 2 km far from the red mud lakes.

4. Due to the long distance between the alumina plant and the disposal area, and the coarse particle size of the roasted mud - the red mud slurry is diluted to a very low, approx. 25 wt %, solid content by recycled water. At present, this fact does not influence the equilibrium of water balance of the alumina plant, however, without modifying the red mud disposal system the quantity of waste can not be reduced.

5. Since only 50 % in average of the Bayer red mud is processed further in the Roasting line there is also a heavy Al₂O₃ loss which is proportional to the mud quantity directly pumped to the lakes.

Recommendations

1. To prepare a Feasibility Study with the main objectives below:

- To improve the water balance of the alumina plant with special emphasis of
 - = modifying the bauxite/liquor slurry preheating system in order to increase the recuperation temperature from the present temperature of 140°C to 190-200°C. This itself can reduce the live steam requirement by approx. 50 % (Figure 2a)
 - = improving the whole digestion system by using indirect heating system for the Bayer digestion.
 - = optimizing the operational parameters of the washing lines (mud level, solids concentration in underflow, overflow clarity, usage of settling aids, measurement and control of operational parameters) in order to minimize both the caustic and Al_2O_3 losses or by other words to minimize the quantity of wastes to be disposed.

2. To prepare a Feasibility Study with the main aim of reducing the environmental hazards from the red mud ponds. In this study the possibilities/conditions of the implementation of the dry red mud stacking system are to be investigated in 2 ways:

- pumping of the thick mud (solid content about 50 wt. %) by high pressure pump

- pumping of red mud slurry in the present state to the disposal site, and at the spot thickening the mud slurry to about 50 wt % solid content by using high concentration/deep thickening technologies.

3. The isolation of waste leakages through the sealing layer of the red mud ponds has been already started by high pressure pumping of concrete into the underground caves/channels. By this activity 90 % of leakages is reported to be blocked, therefore, this kind of work is proposed to continue in the future since at present this is the only solution to avoid/reduce the environmental hazards.

INTRODUCTION

The present Final Mission Report was prepared by J. Steiner and T. Kálmán in connection with Post No SI/CPR/92/802/11-52/JI 3207 and SI/CPR/92/802/11-53/JI 3207 which are attached as Annex Ia and Ib and based on the mission to Guizhou Alumina Plant and Beijing.

The duration of field mission was 6 working days, in China beginning on 4th October and ending on 11th October, 1993, than it was followed by one week home base work.

During the field mission, in accordance with the original job descriptions, the consultants reviewed/discussed the present state/condition of the alumina technology and red mud disposal process in Guizhou Alumina Plant.

Duties fully attained are:

- review/advice on reduction of the amount of red mud to be disposed and its soda content;
- review/advice on the improvement of the material and water balance;
- review/advice on the improvement of the alumina technology applied;
- advice on research on the environmental impact from red mud pumping and establishment of an environment monitoring system
- advice on the study and analysis of chemical and analysis properties of red mud.

Duties partly attained are:

- advice on red mud pumping site selection and construction
The possibility of the establishment of a new red mud pond was said to be marginal, therefore this question was practically taken out from the detailed discussions.
- advice on selection of equipment
This topic mostly relates to the Geho pump expert, who has measured but not evaluated yet the properties of the red mud to be handled. The selection of equipment is possible after having the measurements evaluated.
- investment cost and implementation time estimate

1. INTRODUCTION OF GUIZHOU ALUMINA PLANT

The Guizhou Alumina Plant is basically a consecutively combined alumina plant where the red mud produced by the Bayer technology is a component of the feedstock materials for the roasting/sintering process:

/Figure 1./

Main establishments relating to the alumina plant are:

- 2 bauxite mines. From one of the mines good quality of bauxite is mined out for the Bayer alumina refinery line. Bauxite originates from the other one is used as a component of feedstock materials for the sintering process.

The chemical compositions of the bauxites are summarized in Table 1.

<u>Main</u> Components	<u>High grade bauxite</u> (Bayer quality)	<u>Low grade bauxite</u> (Sinter quality)
	wt. %	
Al ₂ O ₃	70.3	55.8
Fe ₂ O ₃	2.4	4.0
TiO ₂	3.5	2.6
SiO ₂	7.5	16.7
CaO	1.3	4.2
L.O.I.	14.6	15.0

Table 1. Bauxite compositions; Average of 1992

- limestone mine from where the required quantity of limestone is supplied for both the Bayer and Sinter processes.
- alumina plant with rated production capacity of 400000 tpy. This production level has not been achieved to date. The actual production level is approx. 300.000 tpy. Both sandy and floury type of alumina are produced. The proportion of alumina produced by Bayer and Sinter technology is about 55 to 45 % resp.
- aluminium electrolysis plant with the production capacity of 190.000 tpy metal in the form of ingots.
- The number of employees are: 22.000

The alumina works is situated in a very nice mountainous environment where several lakes and rivers can also be found. As far as the climate is considered, it is a subtropical climate, with the lowest temperature of about 0°C and the highest one of above 30°C.

2. THE PRESENT STATE OF THE ALUMINA PLANT

Bayer alumina refinery

The building of the Bayer alumina refinery was started in 1958 and was put into operation in 1978.

The Bayer production line includes the following technological steps:

Bauxite grinding

The crushed bauxite (average grain size: 25 mm) is fed into the grinding mills along with the burned lime and digesting liquor having 220-230 gpl Na_2O content where the bauxite is ground below 100 μm . For grinding there are 3 mills out of which 1 to 2 are in operation and the rest is standby.

The main sizes of the mill are:

Diameter: 3200 mm

Length : 3100 mm

Capacity: 44 tph each

Bauxite/liquor slurry preheating and digestion

The technological flow diagram is shown in Figure 2.

According to the digestion technology applied 4 digestion lines, including 9 autoclaves in each line, are used for the digestion of bauxite slurry. The sizes of the autoclaves are the followings:

- Diameter: 1.6 m

- Height : 13.5 m

Each digester line is connected with a preheating line including 8 pcs of two ways preheaters.

The preheaters are heated by flash steam originating from the flash tanks.

Each digestion line is connected with 3 flash tanks.

Main features of digestion operation:

- the bauxite/liquor slurry is fed into the system by high pressure piston pumps. There are 6 pumps (capacity: 60-85 m³/hr slurry; end pressure: 65 bars) out of which 3 are in operation and the rest are standby or under maintenance.

- the Na₂O content in this condensate water (ranging between 15 to 40 gpl Na₂O, while the same at normal process conditions is 0.5 to 1 gpl Na₂O) shows the flashing system operation is ^{not} ~~pure~~ and deteriorates the red mud washing, too.

- the preheated slurry is sent to the digester line where the slurry is further heated to 240°C using direct live steam heating. The pressure of the steam is 35 bars.

- the digested slurry gets into the flashing units where the temperature of the slurry drops down to the required temperature (no exact data are available in the plant).

Dilution, settling and red mud washing

The digested, cooled slurry is diluted from the caustic content of about 190 gpl Na_2O to approx. 140 gpl Na_2O content by using the overflow of the first washer.

After dilution, the slurry is fed into the thickeners for the separation of red mud from the pregnant sodium-aluminate-solution.

For the red mud separation 2 settlers are used having the following features:

- 5 chambers, conical bottom types
- Diameter: 16.0 m
- Height : 11 m

The underflow from the settlers is fed into the red mud washer system which includes 5 operating units featuring by the same parameters as the settlers.

One unit serves as standby for both settlers and washers.

The washing system applied is shown in Figure 3. while the Na_2O concentrations characterizing the digestion, dilution and washing line are shown in Table 2.

From data of Table 2. it is clear that the operation of the washers is far away from a normal operation state and the washing efficiency is estimated to be 50 % compared to a normal (optimal) washing yield.

The reasons of this poor situation can be:

- uneven and extreme underflow discharges from both the settlers and washers
- the high caustic content of the wash water which originates from the alkaline condensate water and from the recycled pond water.

Red mud filtration and disposal

The underflow from the 5th washer is filtered by 8 pcs of vacuum drum filters having the following technical features:

- surface : 40 m²
- capacity : 7 t/hr dry mud
- solids content
of filter cake : 50 wt. %

The filter cake is washed on the surface of filters by hot wash water. however, the washing efficiency is very doubtful as fresh water can hardly be used and the other components of the wash water is heavily contaminated with caustic.

The filtered cake than repulped by recycled water and 50 % of the red mud slurry (solids content: 20 to 30 wt %) is pumped through 3 pump station to the red mud pond and the rest is used up in the sinter process.

The proportion above is changing time to time and depending on the operation conditions, at times 100 % of the slurry is pumped into the lake.

This fact, apart from the heavy caustic losses causes also a significant Al₂O₃ losses both in solid and liquid phases presenting an additional mud loading on the red mud reservoir. The particle size distribution of the red muds are shown in Table 3.

Alumina production by sinter process

The sinter production line was put into operation in 1988.

The main technological steps of this process are:

Sintering, grinding/leaching

The principal of this technology is shown in Figure 1.

According to this, the red mud slurry from the Bayer line is mixed with low grade bauxite, limestone and sodium carbonate solution.

The mixture is fed into the sintering kilns fired with concentrated coal. The desired reactions take place at about 1100-1200°C.

There are 3 pcs of kilns at disposal with the parameters below:

Diameter: 4 m
Length : 90 m
Capacity: 1080 tph

After sintering, the sintered material is fed into the attack mills where the grinding and decomposition of the sintered material take place at the same time.

The parameters of these mills are:

Diameter: 2.4 m
Length : 13.0 m
Capacity: 31 tph

Separation, red mud washing and disposal

For the separation of red mud and for the washing of the same 6 pcs. single chamber equipment with conical bottom are at disposal. In general 5 units are in operation and one is standby.

The equipment exhibits the following features:

- Diameter: 24.0 m
- Height : 4.5 m

The discharged red mud slurry from the separator unit is fed into the 5 stages washing line where the caustic content of the red mud is countercurrently washed out.

The selected operation data of the washing line are shown in Table 4.

The main operation problems of the washing system here are practically the same as of the Bayer red mud washing line.

There is a significant difference between the two types of mud namely the difference in the particle sizes and particle size distribution (See: Table 3.).

This above, deteriorating the pumping out conditions, namely this mud can be transferred to the lake through 5 pump stations even at 15 to 20 wt % solids content.

Evaporation

In order to maintain the water balance of the alumina plant (i.e. to concentrate the various diluted sodium-aluminate-liquors)

there are 4 pcs of evaporator units at disposal.

The capacity of each unit is 50 tph evaporated water.

Based on the data given by the alumina plant management, by the built in evaporation capacity (i.e. 200 tph evaporated water) the required quantity of water can not be taken out from the alumina plant circuit.

This above means that the accumulation of water in the red mud ponds is being continued.

Red mud disposal

The two red mud ponds are situated on a karstic ground and valleys. One of the ponds serves to receive the red mud produced by the Bayer technology and other is for disposing the red mud from the sinter process.

The distance and level difference between the alumina plant and the disposal areas are shown in Figure 4.

The ponds are heavily loaded with high alkaline containing water the quantity of which is roughly 1.5 million m³ having the caustic content of 12 to 15 gpl Na₂O along with 6-8 gpl soluble Al₂O₃ content.

This huge amount of diluted liquor, on one hand is very harmful for the environment, however, on the other hand it also represents a heavy loss in money the extent of which is roughly 6 million USD. On the basis of the present data the yearly increase of the losses is appr. 0.5 million USD.

At present, the most serious problem at the red mud lake that the alkaline containing waste is penetrating through the sealing layer of the lakes contaminating the underground water reserves.

The extent of the contamination is significant which can be characterized by pH values. This pH value is appr. 9 even at 1 to 2 km distance from the mud lakes.

The quantity of the water disposed is further increased by the rain falls the amount of which can not be estimated as data on the yearly average rain falls have not been available at the site.

These problems above can be reduced by the following ways:

- the contamination of underground water can only be reduced by special post sealing methods, namely by pumping sealing material into the ground where the contamination is observed.

This kind of sealing has been started by pumping concrete into the underground caves/channels.

The effectiveness of this work is said to be 90 %.

- it would be important to eliminate the rain water incoming to red mud ponds at the earliest.

The solutions should be directed both to eliminate of rain water flowing down on the hills slopes and the rain water penetrated into the underground of the hills slope and is interconnected with the underground water of the lakes.

The elimination of rain water can be realized by the erection of dams which has to be preceded by a careful geological survey and dam design work.

- to reduce the Na_2O content of the disposed slurry by decreasing the Na_2O content of red mud wash water and by optimizing the operation parameters of red mud washing lines

- the decrease of the disposed waste water quantity is also crucially important since the higher waste water level promotes the penetration of wastes into the ground water. This above can only be achieved if the evaporation capacity was increased and the present direct steam heating system of the digestion was changed into an indirect heating system.

By these modifications, more waste water could be recycled into the plant than the quantity of water to be disposed - the realization of red mud dry stacking can also ease the situation through the fact that, once the red mud is stored in dry form it will not contaminate the underground water reserves any more.

More details on this can be found in G. van Rijswijk's report who was mainly responsible to investigate this question.

3. Miscellaneous

During the field work we requested to fill in a Questionnaire prepared for the collection of input data of our mathematical model by which the plant problems can be evaluated. Since the requested data were not available we could not conduct such analysis.

We also requested for various samples which were prepared by the plant staff and were taken to ALUTERV-FKI Ltd., for investigation. The chemical and phase composition of samples were determined and the results are given in Table 5. and 6. Since the samples were not representative/collected ones, only qualitative conclusions may be drawn from the results of analysis.

These are the followings:

- the quantity of diaspore remained undigested is changing in the mud samples depending on where the sample was taken from.
This at the same time means that the operation of digestion line is not stable.

- the quantity of lime used for the bauxite digestion seems to be too high and it can cause a high Al_2O_3 losses specially when the Bayer red mud is not processed further in the sinter line.
Therefore, the revision on digesting technology might be very useful.

Budapest, 22 October, 1993

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Bayer process

Requested concentration data

Digester	Na ₂ O ₆ (gpl)	Al ₂ O ₃ (gpl)	molar ratio
Feed slurry	201.37	107.42	3.08
Discharged slurry	196.06	199.41	1.62

Dilution	Na ₂ O ₆ (gpl)	Al ₂ O ₃ (gpl)	molar ratio
Diluted slurry (dry)	5.07	28.06	-
Dilution water	75.1	65.94	-

Settling and washing

Feed of	Na ₂ O ₆ (gpl)	Al ₂ O ₃ (gpl)	molar ratio
1. Thickeners	142.83	138.23	1.70
2. 1st Washer	75.1	65.94	1.87
3. 2nd Washer	65.0	60.91	1.76
4. 3rd Washer	53.61	46.99	1.88
5. 4th Washer	47.65	43.03	1.82
6. 5th Washer	42.23	37.42	1.87
7. Filters	40.20	35.15	1.88

Granulometry of muds (% wt)

	<u>Bayer process</u>	<u>Sinter process</u>
+150 μ	1	9
-150+100 μ	2	2
-100+60 μ	3	5
-60+40 μ	4	11
-40+20 μ	19	33
-20+10 μ	26	27
-10 μ	45	13

Table: 4

Roasting (Sinter) process

Requested concentration data

Feed of	Na ₂ O ₆ (gpl)	Al ₂ O ₃ (gpl)	molar ratio
1. Separator	89.18	101.34	1.45
2. 1st Washer	37.1	48.35	1.26
3. 2nd Washer	28.0	38.42	1.20
4. 3rd Washer	24.0	32.17	1.23
5. 4th Washer	18.0	26.31	1.13
6. 5th Washer	16.0	20.72	1.27

Table: 5
: : : : :

Data of sample analysis

	Moisture	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O
High quality bauxite (*)	-	19,6	6,2	66,1	2,1	3,1	0,5	0,5	-
Slurry after grinding	0,5	16,7	5,3	56,3	1,8	2,65	14,5	0,4	-
Slurry after dilution	0,8	13,7	15,8	22,9	5,0	7,4	25,7	0,8	6,0
Slurry after filtration	0,8	14,0	14,8	26,9	4,8	6,3	23,6	0,7	5,9
Sinter slurry after washing	3,2	8,7	22,2	11,0	5,6	4,3	39,7	1,1	4,1

(*) calculated

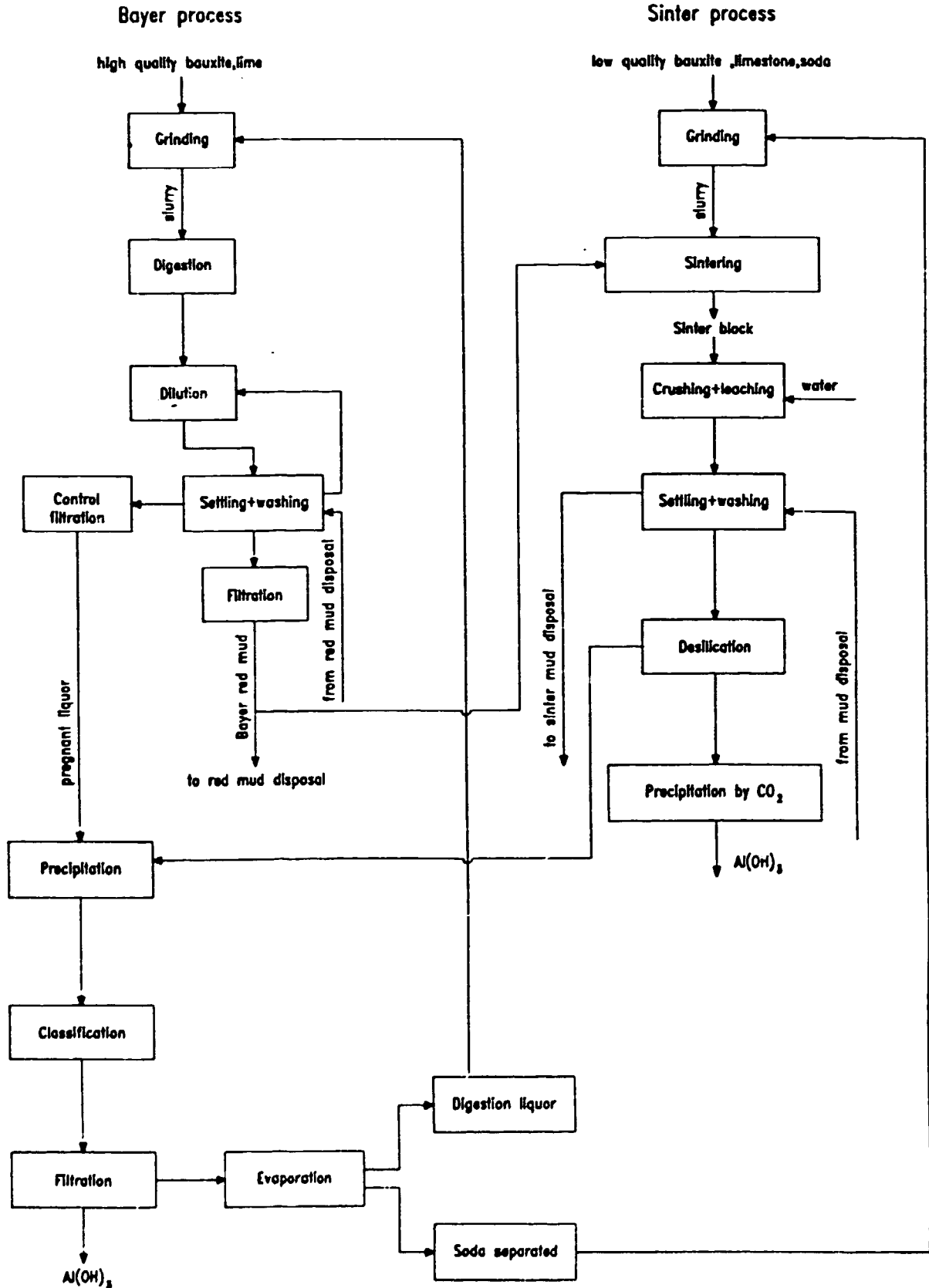
Table: 6

Phase analysis

Phase	Slurry after grinding	Slurry after dilution	Slurry after filtration	Sinter slurry after washing	
<u>Al₂O₃</u>	diaspore	44.2	2.1	6.4	-
	boehmite	0.5	-	-	-
	kaolinite	3.7	-	-	-
	CAS	7.9	13.4	11.7	4.2
	gibbsite	-	-	1.5	-
	NAS	-	7.4	7.3	3.3
	3CaO·Al ₂ O ₃ ·3SiO ₂	-	-	-	3.5
Σ	56.3	22.9	26.9	11.0	
<u>CaO</u>	CAS	13.0	22.0	19.3	6.9
	Ca(OH) ₂	0.5	-	-	-
	CaCO ₃	1.0	0.9	1.0	2.5
	CaTiO ₃	-	2.8	3.3	3.0
	3CaO·Al ₂ O ₃ ·3SiO ₂	-	-	-	5.8
	2CaO·SiO ₂	-	-	-	21.5
	Σ	14.5	25.7	23.6	39.7
<u>SiO₂</u>	kaolinite	4.4	-	-	-
	CAS	0.9	7.1	6.2	0.6
	NAS	-	8.7	8.6	3.9
	2CaO·SiO ₂	-	-	-	11.5
	3CaO·Al ₂ O ₃ ·3SiO ₂	-	-	-	6.2
Σ	5.3	15.8	14.8	22.2	
<u>TiO₂</u>	anatase	2.4	3.4	1.6	-
	rutile	0.3	-	-	-
	CaTiO ₃	-	4.0	4.7	4.3
Σ	2.7	7.4	6.3	4.3	
<u>Fe₂O₃</u>	hematite	1.3	4.3	4.1	0.4
	goethite	0.5	0.7	0.7	-
	Na ₂ O·Fe ₂ O ₃	-	-	-	5.2
Σ	1.8	5.0	4.8	5.6	
<u>NaO₂</u>	NAS	-	6.0	5.9	2.7
	Na ₂ O·Fe ₂ O ₃	-	-	-	2.0
Σ	-	6.0	5.9	4.7	

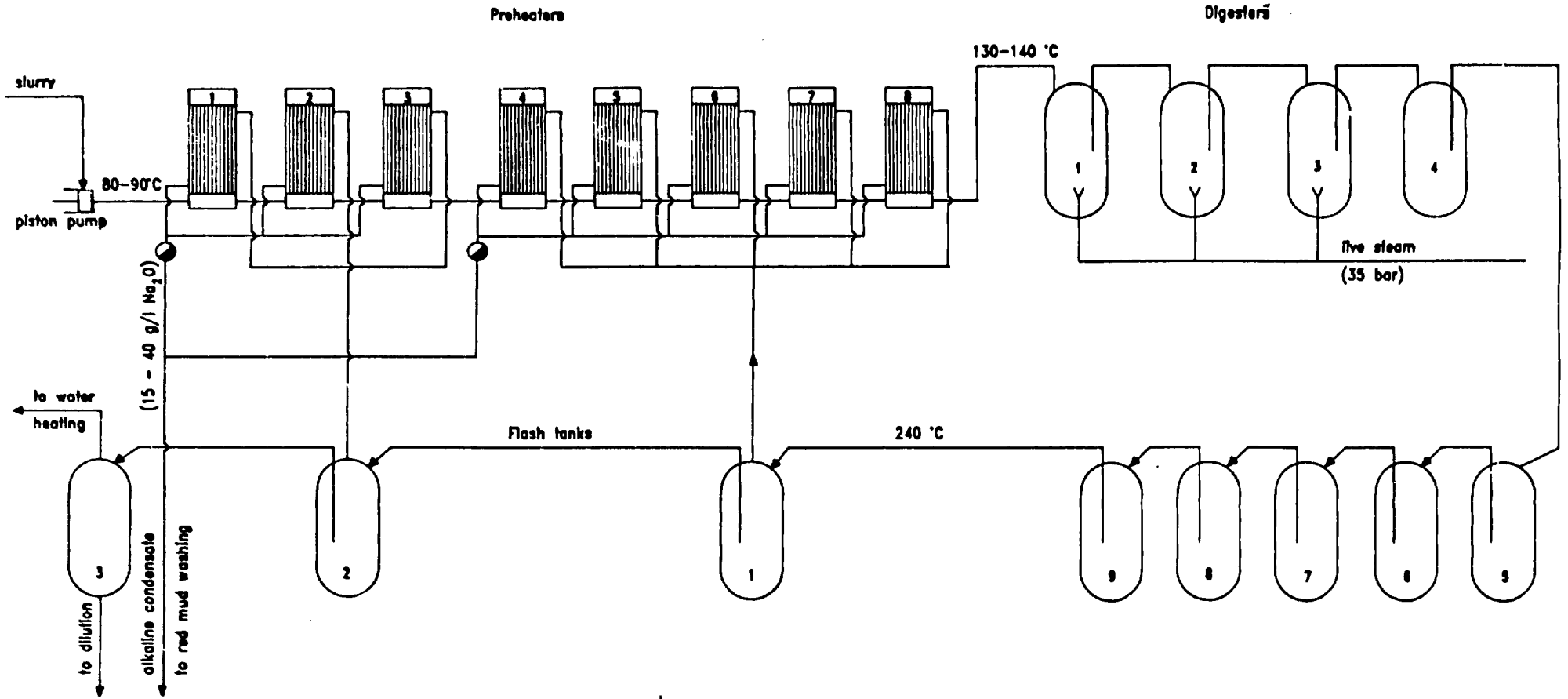
ALUMINA PROCESS FLOWSHEET-SCHMATIC OF THE GUIZHOU ALUMINA REFINERY

Fig.1



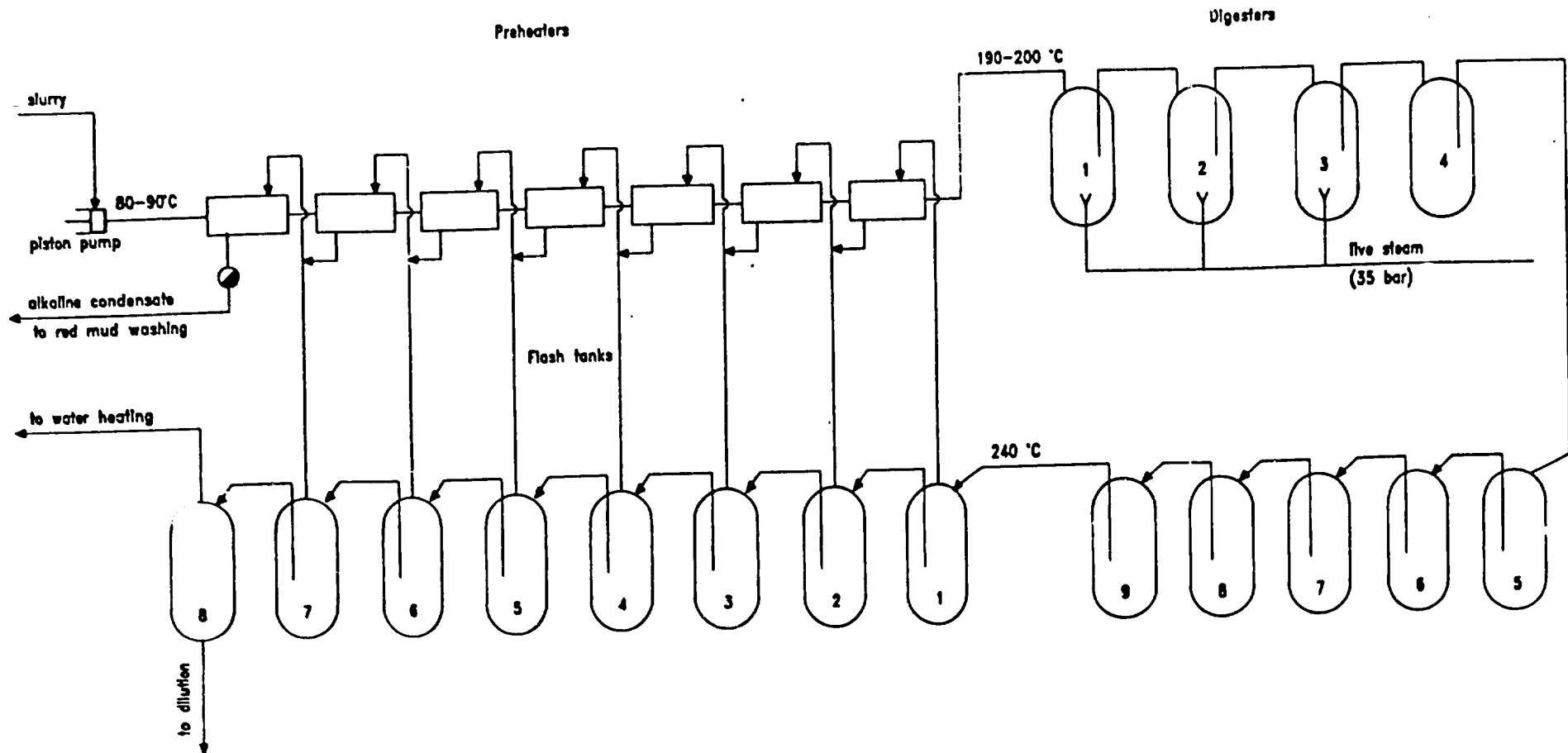
PROCESS FLOW DIAGRAM OF DIGESTING LINES

Fig.2



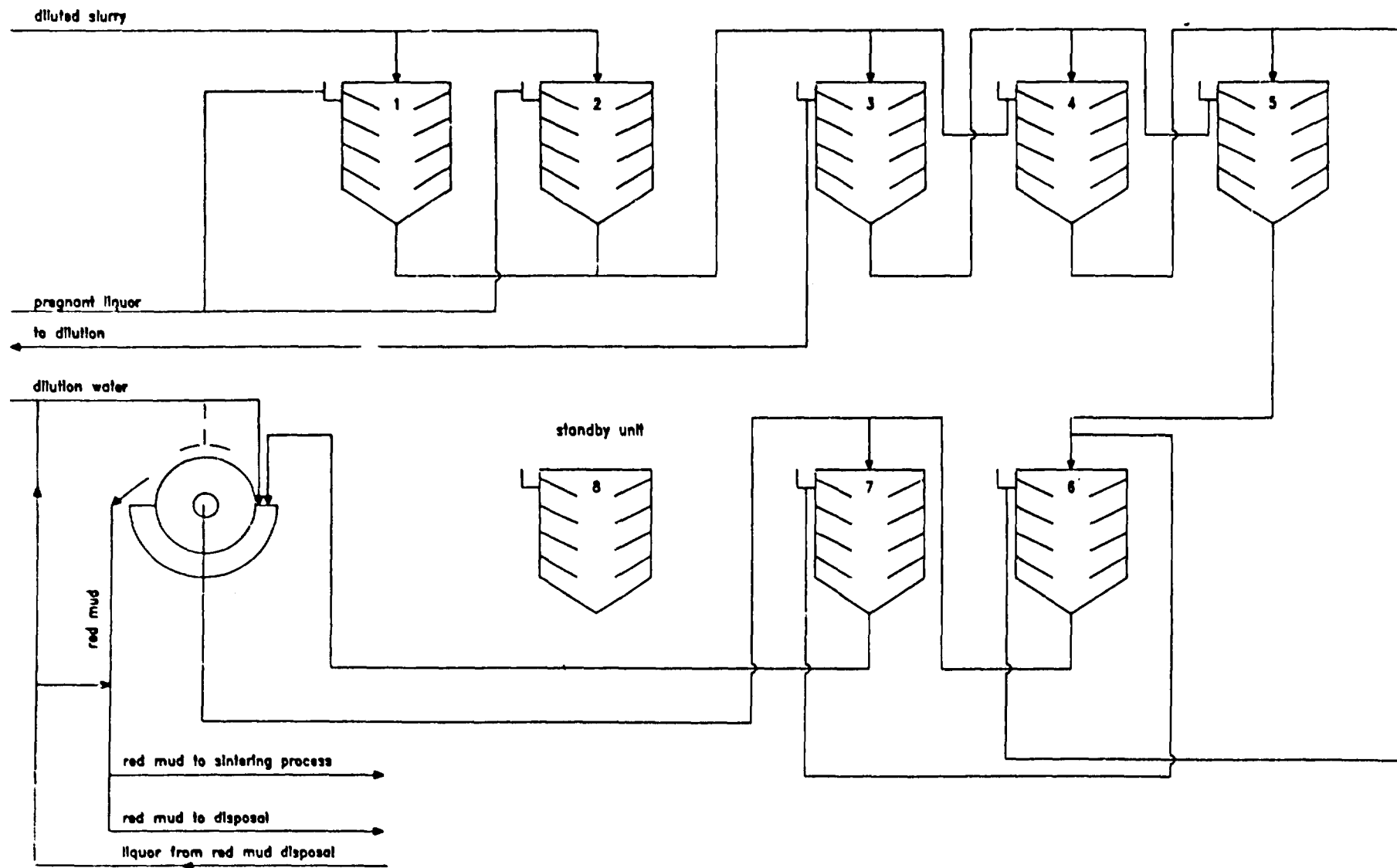
PROCESS FLOW DIAGRAM OF DIGESTING LINES
(Recommendation)

Fig.2 e



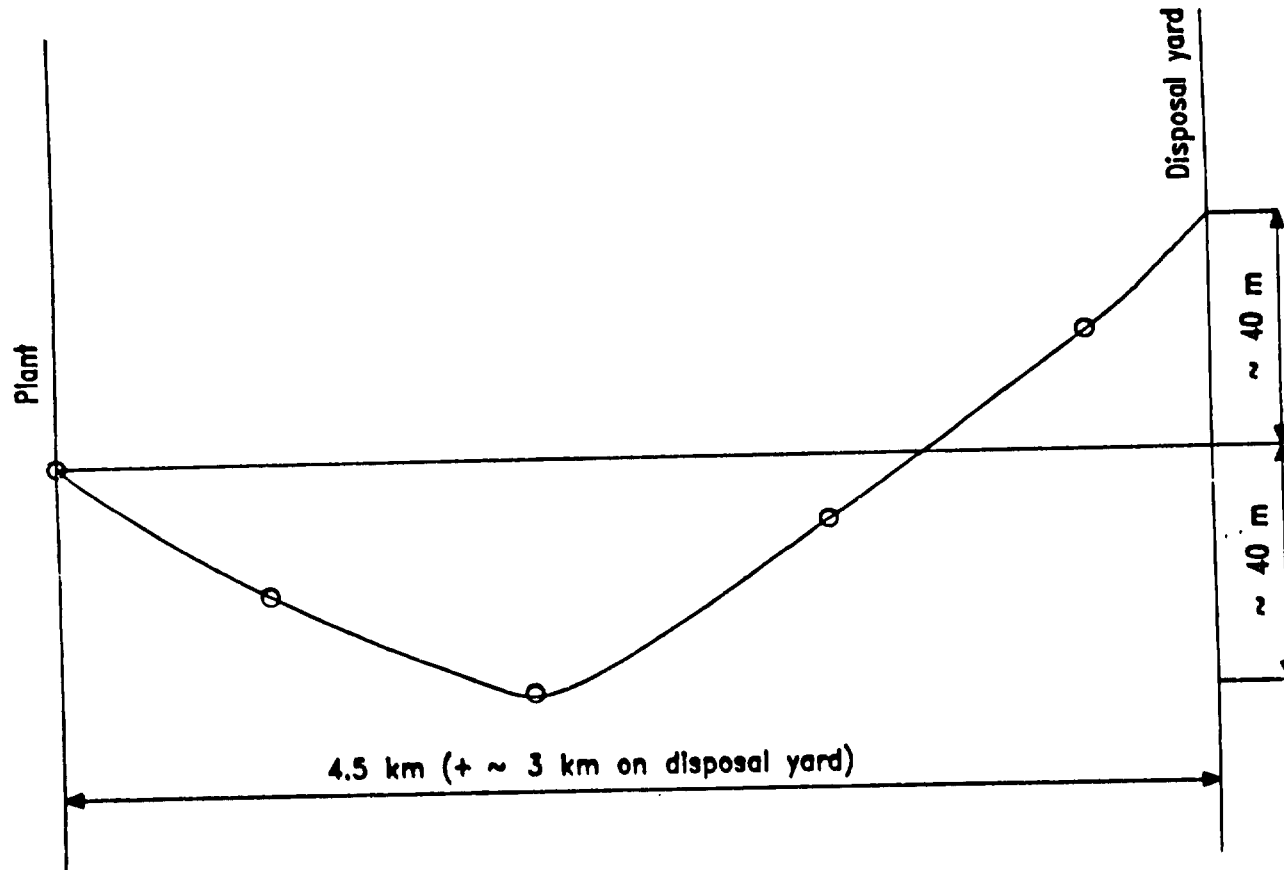
PROCESS FLOW DIAGRAM OF RED MUD SETTLING, WASHING AND FILTRATION

Fig.3



Distance and level difference between Plant and Disposal

Fig.4



○ Pump station

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

JOB DESCRIPTION

SI/CPR/92/802/11-52/J13207

Post Title: Consultant in red mud treatment and disposal technology

Duration: 2 weeks total, which includes 1 week in the field and 1 week service at home base for collection of information and preparation of final mission report.

Date required: September 1993

Duty Station: Beijing and Guizhou Alumina Plant

Purpose of project: To provide CNNC and Guizhou Alumina Plant with high level consultancy service, which will assist CNNC and the National Environment Committee in evaluating different technology choice in red mud handling and processing.

Duties:

During his field mission, the expert will make an in-depth assessment/analysis of the alumina technology and red mud disposal process in Guizhou Alumina Plant and present proposals for its improvement including:

- advice on red mud dumping site selection and construction technology;
- advice on red mud treatment and disposal technology;
- advice on selection of equipment;
- investment cost and implementation time estimate;
- advice on establishment of an environment monitoring system; and,
- advice on the study and analysis of chemical and physical properties of red mud.

Applications and communications regarding this Job Description should be sent to:

Project Personnel Recruitment Section, Industrial Operations Division
UNIDO, VIENNA INTERNATIONAL CENTRE, P.O. BOX 300, Vienna, Austria

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

JOB DESCRIPTION

SI/CPR/92/802/11-53/J13207

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Duration: 2 weeks total, which includes 1 week in the field and 1 week service at home base for collection of information and preparation of final mission report.

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- advice on the study and analysis of chemical and physical properties of red mud;
- advice on the improvement of the material and water balance;
- advice on the improvement of the alumina technology applied; and,
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Project Personnel Recruitment Section, Industrial Operations Division
UNIDO, VIENNA INTERNATIONAL CENTRE, P.O. BOX 300, Vienna, Austria

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