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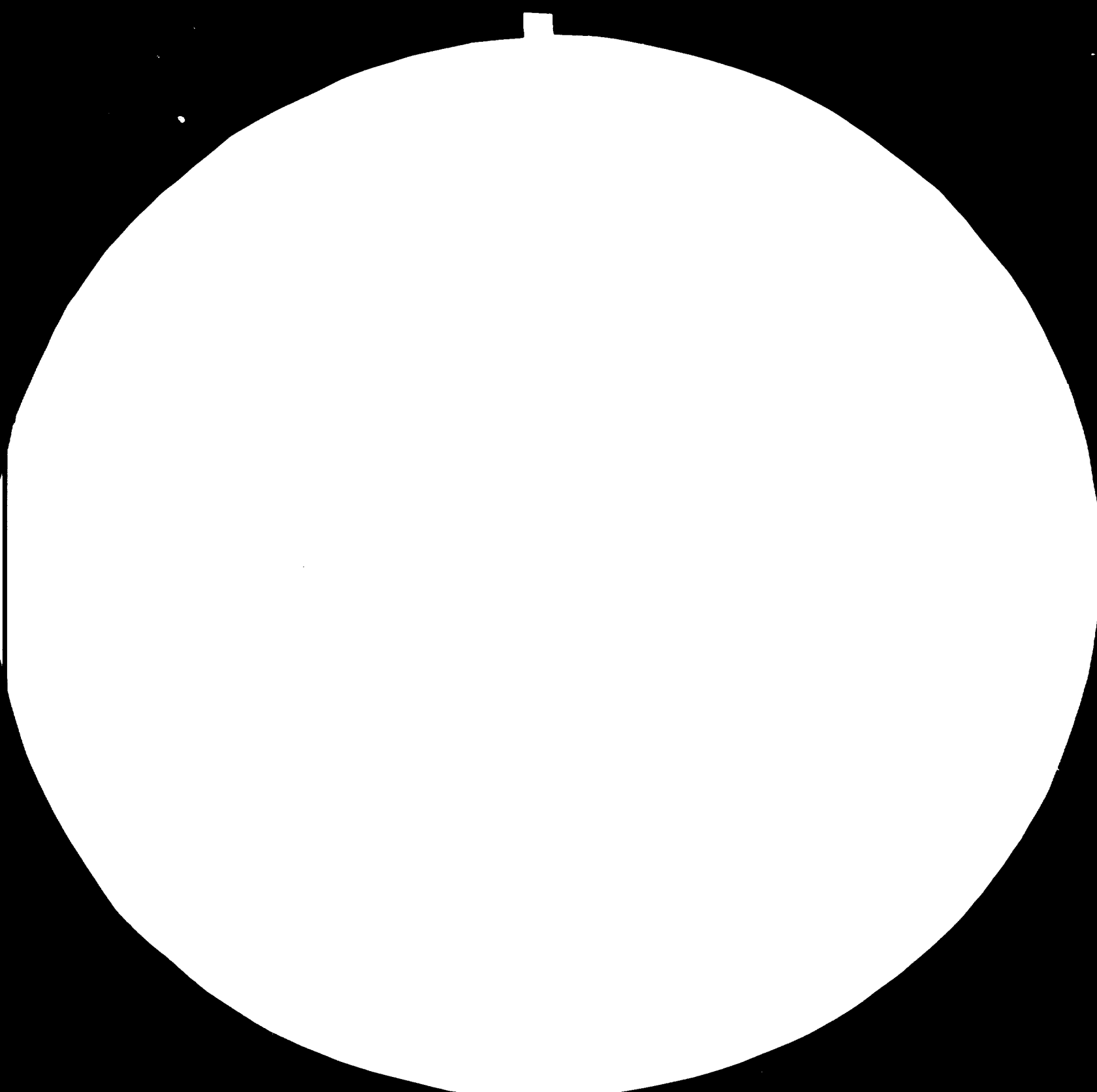
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MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL NO. 1010
APPLICABLE TEST METHOD: NBS 1010



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

13553

IMPROVEMENT OF ANODE PERFORMANCE
for the
ALUMINIUM SMELTING IN INDIA

FINAL REPORT

SI/IND/82/801

authors →

ALUTERV-FKI
Budapest/Hungary
March, 1984

India.

1987

IMPROVEMENT OF ANODE PERFORMANCE

for the

ALUMINIUM SMELTING IN INDIA

Project No. SI/INC/82/801

Final Report

by

ALUTERV-FKI as foreign consultants

dr. J. Horváth	Head of Team
Mr. T. Ferenczi	Chem. Eng./R and D
dr. F. Mosóczy	Chem. Eng./R and D
Mrs. Zs. Pálovits	Chem. Eng./R and D

with assistance of

BALCO as Indian consultants

Mr. P.N. Sharma	Works Manager National Project Coordinator
Mr. P.K. Gairola	Assistant Superintendent (Smelter)

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Improvement of Anode Performance in
Aluminium Smelting in India

1. INTRODUCTION

1. INTRODUCTION

1.1 Background

The BALCO KORBA Aluminium Plant operates aluminium electrolysis cells of an amperage of 100 KA, equipped with Soderberg type anodes which are formed continuously in regular periods of time. One of the problems occurring widely during the operation is the uneven consumption of the anode bottom surface submerged in the molten salt electrolyte, with coke particles of the anode crumbling from this surface and all around the lower half of the anode body. The result is the necessity to "skim" the coke particles in regular intervals from the surface of the molten electrolyte, causing thereby losses of carbon and electrolyte and degrading significantly the working conditions of the operators. The significant formation of the "Carbon froth" in the cell is one of the well known disadvantages of the Soderberg type of anodes against the "prebaked" type.

During the conference of ICSOBA (International Conference on Studies on Bauxite and Alumina) held in October 1981 in Hungary it was published that by appropriate utilization of salt additive of catalytic effect to the anode paste the quality of the anode surface improves significantly and the quantity of "skimming" decreases by 50-75 %, resulting in sizeable reduction of consumption of carbon and electrolyte and consequently production costs. The working conditions and the quality of metal produced improve too. This method of improvement may be readily transferred to India by assignment/fielding of a team of experts by a subcontractor, experienced in this specific technology, to elaborate and implement in co-operation with the Indian counterpart and on a group of experimental electrolysis cells the method and technology as applied to the local conditions.

1.2 Literature Review

The effect of several materials has previously been studied under laboratory conditions in order to improve the quality of self-baking anode paste, to decrease its specific consumption and to decrease crumbling (carbon scum). The following were the targets at selecting the quality and quantity of the dopes:

- its quantity should not significantly increase anode resistance;
- its quality should not pollute the metal produced, should not impair the technological parameters of the electrolysis (the alumina solution power, density, viscosity, and overheating of the electrolyte), should not reduce current efficiency (mainly application of boron and aluminium compounds);
- it should not be detrimental to the working place and its environment.

The used inorganic additive changed mainly the quality of the binding material (softening point, amount and reactivity of coking residue). This occurred whether the additive has been added to the binding material before production or during paste production as additive.

The real laboratory studies on the effect of additive begun in the Research Institute for Nonferrous Metals in 1968. In the study about the mechanism of the effect of several dope materials, the self-baking anode paste containing 0.5-1.0 % anhydrous AlF_3 was found to be the best. This, without undesirable metallurgical side effects, decreased formation of carbon scum by about 50 %, increased current efficiency by nearly 1.5 %, decreased specific electric energy consumption on the average by

180 kWh/t, increased production of metal with lower than 0.06 % Si content and decreased specific anode paste consumption on the average by 7.2 kg/t. This anode paste has been used in the hungarian aluminium smelters of vertical stud anodes between 1972-1982 and in some smelters of the Soviet Union since 1976, according to Hungarian Patent (basic number FE-812, application number 160 683), which is the joint property of FKI and VAMI.

Several authors have studied inhibitors decreasing anode consumption in the last 25 years. Their measurements were usually restricted to the determination of the degree of inhibitor effect. Usually neither the mechanism of the effect nor the effect of additive on the electrolysis technology was studied.

According to the norwegian patent (No. 92060, A/S Ardal og Sunndal Werk) (1), which was published in 1958 the undesirable effect of vanadium content can be neutralized by adding 0.3-0.5 % boron compound to the coke during production.

F. K. Earp and M. W. Hill (2) reports about the inhibitor effect of some phosphates and borates at the oxidation of carbon and graphite caused by air.

G. Wrangler (3) has used B_2O_5 , P_2O_5 , $Na_2B_4O_7$, Al_2O_3 and AlF_3 dopes in order to decrease the non-electrolytic oxidation of binding coke material. B_2O_3 and P_2O_3 proved to be most effective. 0.5 % dope reduced oxidation to one tenth.

According to the patent USP No. 3 442 787 (4) Li, Be, B, Na, Mg, Al, K and Ca oxides, their mixtures and their halogen compounds, added to the fine fraction of the coke material in 0.1-3 % amount, decrease specific anode mass consumption during aluminium electrolysis.

According to the english patent EP No. 177 829 (5), specific consumption of anode carbon is decrease and current efficiency is increased in effect of adding 0,5-5 % of CaCO_3 , Al_2O_3 , LiF , CaF_2 or Na_2CO_3 during the production of self-baking mass.

In the second half of the sixties G. F. Veder-nyikov and M. M. Vetyukov (6) have added several inhibitors to the binding material. Paste was prepared from pitch coke with 30 % binding material in laboratory and characteristics of baked specimen were studied. Measurements were made on samples with 0.2-2 % B_2O_3 (H_3BO_3) and SiO_2 , 1-3 % $\text{Al}_2(\text{SO}_4/3)$ and AlCl_3 , 0.2-1 % Na_2CO_3 and 1-2 % $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SiO}_3$ dopes.

The oxidation and crumbling in CO_2 flow and anode consumption in bench scale electrolyser were studied, and the electric force was measured. The volumetric weight, real density, porosity, specific electrical resistance and compressive strength of baked specimen were determined.

The best effect was achieved with the use of B_2O_3 and SiO_2 . The oxidative and crumbling loss of samples with Na_2CO_3 dope were sharply increased, while Na_2CO_3 and H_2SiO_3 were ineffective, when both were added.

It was established that inhibitor dopes diminish the activity of coke binding material, thus the oxidation becomes steady, the oxidative and crumbling loss as well as anode consumption decrease.

It was established by electrochemical studies that electrochemical oxidation occurs mainly in the binding material. The activity of the coke treated with inhibitors diminishes, the oxidation of the anode bottom occurs evenly and at the same time overvoltage appears in the anode process. The inhibitors suppress the effect of catalytic components.

Robozarov and Vetyukov (11) added 0.36-8.9 w% H_3BO_3 to the normal coal tar pitch binding material used for paste production. Bench scale anode mass sample containing 0.11-2.7 w% H_3BO_3 was prepared from pure pitch coke, mixtures of pitch coke and petroleum coke in several ratio (85-15 %, 50-50 %, 15-85 %) or pure petroleum coke with the use of such binding material. Based on the studies of baked laboratory size specimen the following were established:

- in effect of H_3BO_3 dope the compressive strength, specific resistance, volumetric weight is increased but porosity is decreased;
- in the case of pastes made from pure petroleum coke or with petrolcoke addition the previously listed features do not, or only insignificantly appear, with the exception of compressive strength, which is increased in this case, too;
- in the case of H_3BO_3 additive in 0.5 % (related to the mass) the oxidation and crumbling values characterizing the decrease in anode consumption are optimal. However the polarization voltage is increased in this case. The oxidation is reduced to about the half, crumbling to about the tenth of the original value.

These bench scale experiments were not followed by pilot plant experiments at that time.

In recent years several authors (7-10) were again engaged studying the effect of catalysts and inhibitors, most completely P. J. Rhédey (7).

He added the dopes into the paste mixer.

Among the dopes studied B_2O_3 , H_3PO_4 , $Na_2B_4O_7$ and AlF_3 decreased the reactivity towards air from the typical 120 mg/cm² hour to 10-30 mg. $LiCl$ and Li_2CO_3 were ineffective, Na_2CO_3 , Na_3AlF_6 and NaF increased the reactivity to 200-300 mg/cm² hour.

It was established that among the inhibitors B_2O_3 and AlF_3 did not increase, while borax and phosphoric acid significantly increased anode consumption.

In the case of horizontal stud Soederberg anodes air oxidation above the crust, where the temperature is 575°C on the average, can be reduced from 7 % to 4 % by adding 5 % AlF_3 (related to coke) and to 2 % by adding 1 % B_2O_3 .

A. Limonchik (9) reports the improvement of the characteristics of pitch coke due to organic phosphorous compounds. Phosphorous compounds added to pitch increase coke residue and the amount of quinoline insolubles, modify the structure of the coke produced decrease its reactivity towards CO_2 and air and decrease its specific surface area.

The characteristics of specimen produced from masses of the same raw material with different additives (flotated carbon scum with 1 % Na content; 0,65 % sulfanilic acid; 1 % AlF_3 ; 1 % $NaOH$; 0.6 % $FeCl_3$ and 0.6 % H_3BO_3) were studied in laboratory size by E. Jankó and co-workers (13). Moreover the behaviour of anode pastes produced from different petroleum cokes and from pitch coke was studied both in laboratory and in plant scale (Irkutsk aluminium smelter). The binding material content of pastes and their deformation, the compressive strength, specific electrical resistance, porosity of the baked

specimen their oxidation and crumbling in CO_2 atmosphere at 950°C , their total loss during electrolysis according to Watanabe and in cryolite melt were studied (at 100 mm diameter, 100 mm long specimen with 380 A current, 2200 Ah). They concluded the followings:

- dopes with Na content increase anode consumption;
- the oxidative and crumbling loss decreased significantly (by 50 %) in the case of pastes with AlF_3 or H_3BO_3 content;
- despite greater (with 3-4 %) binding material content anode masses of petroleum coke without additives showed smaller degree of burning and crumbling than masses of pitch coke;
- it is an experience of the Irkutsk smelter that in the case of the same (83-84 %) current efficiency the specific mass consumption of pure petroleum coke is about with 15 kg/t less than that of pitch coke.

2. TECHNOLOGICAL EXPERIMENTS WITH AlF_3
ADDITIVE IN BALCO-SMELTER

2. TECHNOLOGICAL EXPERIMENTS WITH AlF_3
ADDITIVE IN BALCO-SMELTER

2.1 First Phase of Experiment - Preparation
of Experimental Anode Paste

Referring for the Contract No. 83/6 between UNIDO and ALUTERV-FKI para 2.02/a the Contractor's personnel named in para 2.03/a Dr. Janos Horvath (Team Leader) and Tibor Ferenczi (Specialist) arrived at the Project area (KORBA ALUMINIUM SMELTER) on 23 June, 1983 for carry out the experimental work entitled "Improvement of Anode Performance in Aluminium Smelting".

It covers the following activities in presence of Contractor's Personnel.

- Making detailed programme on "Project"
- Production of total quantity of experimental anode paste required for the completion of experiment
- Selection of experimental as well as reference cells
- Start charging experimental anode paste into the selected cells
- 0.5-0.1 % sampling of produced experimental paste and making composite samples for the purpose of various tests and analyses either in Government's laboratory at KORBA or in Contractor's laboratory at Budapest
- Determination of various technical parameters of experimental and regular anode paste are to be measured or analysed during experimental period

- Determination of various operating parameters at experimental and reference cells to be measured during experimental period
- Collecting, packing and sending to BUDAPEST 4x5 = 20 Kg composite experimental, 5 Kg regular anode paste, 5 Kg pitch and 5 Kg calcinated petrol coke sample
- Collecting and recording of various operating parameters of experimental and reference cells.
Second phase of experimental period from 01-08-1983 to 16-10-1983.

In absence of Contractor's Personnel the following activities would be done by Government's Personnel at Project Area

- Unbroken charging of experimental anode paste into the selected experimental cells
- Performance and record at the specified laboratory tests and analyses on experimental anode paste
- Recording all the determined operating parameters of experimental and reference cells
- The following Home Office Service will be done by Contractor's Personnel at BUDAPEST
- Performance of specified laboratory tests and analysis
- Writing and sending Interim Report to UNIDO Viena
- Determination of aspects for evaluation of experiment

Third Phase of experimental period from 17-10-1983 to 27-11-1983.

- Government's Personnel together with Contractor's Personnel at Project Area will measure and evaluate the effect of aluminium fluoride anode paste on experimental cells
- Measured operating parameters of experimental cells will be compared to the relevant parameters of reference cells
- Government's Personnel and Contractor's Personnel will take part with UNIDO staff on Draft Final Report Meeting in the Project Area - as per Contract para 2.04

Fourth Phase of experimental period from 28-11-1983 to 23-12-1983

Contractor's Personnel will make the Final Report as a Home Office Work at BUDAPEST on the basis of UNIDO's written comments on Draft Final Report.

Contractor's Personnel together with Government's Personnel visited Anode Paste Plant and Aluminium Smelter in the Project Area on 27 June'1983.

After having sufficient information about the technical and operating parameters of Anode Paste Plant and Aluminium Smelter Contractor's Personnel prepared detailed programme of Aluminium fluoride anode paste experiment. The Programme was approved and received by Government's Personnel on 1 July 1983. The programme contents the composition of experimental anode paste, time schedule for production of that sampling and analysis and the performance parameters. Further for analysis and the performance parameters. Further for detailed Application Description was handed over by Contractor's to Government's personnel.

With reference to various paragraphs of application description Contractor's Personnel announced that the quality of anode paste which is being used in Aluminium Smelter was different from that quality of Anode Paste had been used by Contractor with application of which successfully was verified the effect of additive aluminium fluoride.

Comparison of more important parameters
of Anode Pastes

	Parameters of regular paste used by Government	Parameters of regular paste used by Contractor
Porosity %	32 - 36.7	25 - 28
Electric resistivity (ohm mm ² /m)	68 - 114	80 max.
Pitch content %	34.25	28 max. 30 [*]
Softening point of Pitch (°C)	94 - 96.5	72 - 75
Compressive strength of baked sample (Kg/mm ²)	158 - 480	min. 300

Remarks x

Binding material content of rich anode paste whose elongation No. is 80-110 % with calcined petrol coke content max. 31 %.

The binding material content of poor anode paste whose elongation No. is 58-70 % with calcined petrol coke content max. 29 %.

With the application of aluminium fluoride anode paste in the operation of aluminium smelting by the Contractor, the technical parameters of anode paste were

observed as follows:

Plasticity	48 %
Ash content	1.18 %
Volatile content	15,20 %
Solubility in anthracene oil	26,3 %
Results with specimen:	
Bulk density	1.510 g/cm ³
Real density	1.968 g/cm ³
Porosity	23,3 vol. %
Compressive strength	380 kg/cm ²
Specific resistance	74 ohm mm ² /m

As it can be seen from the above data that the technical parameters of anode paste being used by Government differ from relevant technical parameters of normal and aluminium fluoride anode paste having been used by contractor. Accordingly to the Contractor's Personnel's opinion this differences are due to the high softening point as well as the high percentage of applicated pitch in anode paste. BALCO's (Govt) Personnel's stated in this connections that due to the local operation conditions modifications of the composition as well as application of lower softening point pitch was not possible at this stage.

Taking into consideration the difference between technical parameter of anode paste is being used and technical parameters of aluminium fluoride anode paste Contractor's Personnel agreed that the (with Govt Personnel's) main target of this fluoride anode paste experiment would be to verify the improving effect of AlF₃ with the production of anode paste as per BALCO's recent anode paste production technology.

As the anode paste with additive AlF₃ decreases the skimming by improvement of properties of binding ma-

terial Contractor's Personnel stated that with the application of aluminium fluoride anode paste the coking residue of binding material increases.

- Strength compactibility and conductivity of coke formed of binding material would be improved
- Porosity decreases
- Compressive strength improves.

Comparing to properties of anode paste is being used. The value of improvement of technological parameters should be determined by means of measuring on operating aluminium reduction cells. It can be started after 100 days from the date of charging of experimental anode paste to the selected cells. It is calculated from anode consumption (15 mm/day) and high of anode (1500 mm).

View points for selection of experimental cells Contractor's Personnel suggested for carry out the experience on 50 (51) Nos. of cells located in one cell house as measuring of experimental anode paste and well separated storage of skim would be satisfactory in this case. Experimental operation of 50 Nos. cells required 2700 t experimental anode paste.

Government's Personnel announced that due to inauguration of cells in cell house No. 5 and 6 production and storage of such quantity anode paste raises objections for them. Further for this they suggested to carry out the experimental programme on one section (i.e. 13 Nos) of cells as one section is well separated from operating and skim measuring point of view. Other important factor for selection of experimental and reference cells, they should be nearly same age. Taking into consideration of the above factors parties agreed in selecting cells Nos 340-351 (12 Nos) - section 4) in cell house No. 3 as experimental

and close to these cells No. 327 - 339 (Section 3, 13 Nos) in the same Cell House as reference cells. One of selected experimental cell (No 349) was under reconstruction so that start charging of experimental anode paste was possible for 11 Nos. cells only.

The aluminium fluoride anode paste experimental requires a total quantity of 720 t experimental anode paste. Government's Personnel were requested to produce the total quantity anode paste during the first phase of experimental period in presence of Contractor's Personnel. (23. 06. 1983) - (31-07-1983). In case of Uniform scheduling weekly production of experimental anode paste should be 180 t. Contractor's Personnel declared that production of total quantity experimental anode paste during first phase of experiment is required for all that as they could be able to carry with them 4x5 = 20 Kg composite sample of experimental anode paste to BUDAPEST where in Contractor's research laboratory those measurements and analysis would be done which were more important for evaluation of experimental programme and in the Contractor's research laboratory could not be done at present. For purpose of doing further measurements and analysis Contractor's Personnel will carry with them raw materials of anode paste i.e. 5 Kg petrol coke and 10 Kg binding material are being used for preparation of regular paste.

On the basis of approved experimental programme and application description - handed over for Government's Personnel earlier production of experimental anode paste started on 01 July '83. Main technological parameters of anode paste production.

Batch composition:

Coke fractions (total)	1955 Kg
Binding material (34.25 %)	1027 Kg
AlF ₃	<u>18 Kg</u>
Total	3000 Kg

Coke fraction:

Fine	40 %	400+382	782 Kg
-14 + 48	20 %		391 Kg
- 3 + 14	40 %		782 Kg
Total			<u>1955 Kg</u>

Charging of these coke fractions as well as binding material into the gauging tank (hopper) was automatically controlled while charging of AlF_3 occurred manually after measuring it by means a hanged scale.

Dry mixing and preheating time of coke fractions and AlF_3 was 20 min. Mixing time of dry heating was going on.

Temperature of mixed material was 145-165°C with application the above technological parameters a quantity of 27 t experimental anode paste was produced on 1st July 1980. The planned quantity could not be produced due to interruption of steam supply.

The produced experimental anode paste was stored on a separated place in anode paste storage after it was bagged and transported to Cell House No. 7 for storage purposes.

Charging of experimental anode paste to the selected experimental cells started on 03-03-1983.

Two samples of the first day produced experimental anode paste was analysed at Government's Laboratory. Results of that was the following:

Anode paste with AlF_3 addition

Analysis	Sample No.1	Sample No.2
Plasticity %	60.61	59,78
Fluidity Ratio	2.41	2.22

Analysis	Sample No.1	Sample No.2
V.M. of Paste	13.45	13.40
V.M. of Pitch	44.58	44.31
Pitch content % (Calculated)	30.17	30.24
Ash %	0.50	0.52
Softening point of corresponding pitch	94°C	95°C

After having the analysis results of the first day produced experimental anode paste Government's Personnel announced their comments on it. Due to the longer mixing period (20 + 40 min) and taking into consideration of interlocks connections of various equipments of Anode Paste Plant the outcome reduced from 14 t/h rate to 6 t/h actual rate.

At this capacity production of experimental anode paste within the period specified in programme is not possible as production of regular anode paste is also should be going on.

- Plasticity of experimental anode paste is less than plasticity of regular anode paste
- Concluded from ash content (0.50 %) the AlF_3 content is less than the calculated one
- Pitch content (determined by calculation) is low

Government's Personnel opinion on the above was that the deviations were caused by longer preheating and mixing time. Further to this they requested Contractor's Personnel to reduce preheating and mixing time having been given in "Application description". In

reply Government's Personnel expressed that the longer mixing time is required for purpose of production homogenous experimental anode paste.

Government's Personnel stated that with mixers applied were modern two arms sigma type ones having good mixing efficiency and homogeneity of mixture could be assured at shorter mixing time too. Mixture homogeneity could be cleared by analysing more samples of experimental anode paste.

Basically technology of anode paste production could not be changed according to the request of Contractor's Personnel. Their request tended towards increasing of mixing time to the interest of securing homogenous distribution of AlF_3 in the manufacture experimental anode paste. Parties finally agreed in a second best solution that production technology of experimental aluminium fluoride anode paste would be the same, as the production technology of regular anode paste being applied - with addition of 21 Kg AlF_3 in place of 21 Kg fine coke fraction.

It was observed that Government's laboratory analysis methods show difference in some cases from detailed analysis methods given in "Application Description" handed over to Government earlier.

After above mentioned discussions composition of experimental anode paste was modified as per the followings.

Batch Composition:

Coke fractions (total)	1952 Kg
Binding material (34.25 %)	1027 Kg
AlF_3	21 Kg
Total	<u>3000 Kg</u>

Coke fractions:

Fine	40 %	400+370	779 Kg
-14+48	20 %		391 Kg
- 3+14	40 %		782 Kg
Total			<u>1952 Kg</u>

Dry mixing and preheating time	5 min.
Mixing time during pitch charging	5 min.
Mixing time (Pitch+Coke+AlF ₃)	<u>30 min.</u>
Total	40 min.

Temperature of Mixture: 145-165°C

With application of the modified technological parameters 23 batches equal to 69 t experimental anode paste has been produced on 06 July 1983. The planned quantity could not be produced due to interruption of steam supply and equipment break-down.

14 batches equal to 42 t experimental anode paste has been produced on 07 July 1983.

It was agreed that samples of three days production (27+69+42 = 138 t) would be handled together and composite sample marked I, would make from that.

Experimental anode paste production on 09 July 1983 was 105 t on 10 July 1983 156 t - total two days production 261 t. Composite sample marked II would be made of this quantity.

Samples of 9 t produced experimental anode paste on 11 July 1983 would be part of composite sample marked III.

Government's Personnel announced on 13 July 1983 that on the basis of laboratory analysis results of composite samples marked I, and II as well as observation on

anode top of experimental cells the plasticity value of produced experimental anode paste was lower than required. Due to this operationing troubles and lower efficiency might come on experimental cells in the course of experimental period.

Contractor's Personnel and Government's Personnel expressed that the lower plasticity of manufactured experimental anode paste had not been caused by AlF_3 additive, further the laboratory analysis reports on experimental anode paste samples had shown significant deviations.

Taking into consideration that all of laboratory tests and analysis specified in Application Description has not been done so far due to lack of some measuring and controlling instruments at Governments laboratory. Contractor's Personnel gave the following suggestions:

- To produce the remaining quantity experimental anode paste with production technology of regular anode paste by charging 21 Kg AlF_3 into one anode paste mixture
- Binding material content is to be increased so that the plasticity of experimental anode paste would reach the value of binding material content in regular paste (34.5 %)
- For Government's Personnel accept the Contractor's analysis results of experimental anode paste samples. Contractor's analysis methods fill requirement of standards. In order to this the quantity of sample should be increased. (10 Kg binding material and 2 Kg of AlF_3).

It was learned that management of Smelter has been searching the proper composition of anode paste with application of high softening point binding material.

This requires more experimental work and application of adequate examination methods - some of them are not available at Government's laboratory at present Contractor's Personnel were requested to assist in this respect.

Parties agreed that the final evaluation of experimental programme would be done on the basis of Contractor's method detailed in Application Description.

27 t experimental anode paste with 34,5 % binding material content was produced on 14 July.

On the basis of laboratory analysis the plasticity of this anode paste (68,54 %) was acceptable. Observation was same on anode tops of experimental cells after charging this anode paste.

Further to this parties agreed that the remaining experimental anode paste would be produced with 34.5 % binding material content and it would be mixed with earlier produced experimental anode paste so that the required plasticity value could be achieved.

The remaining experimental anode paste was produced at the following rates, :

123,6 t	on 20 July 1983
99,0 t	on 21 July 1983
66,0 t	on 22 July 1983
<hr/>	
Total	288,6 t

Production technological parameters were the same as on the previous production day on 14 July 1983.

With production of total required quantity experimental anode paste the most important task of first phase of experimental period has been performed.

Composite sample marked III, was made from $9 + 124,6 = 132,6$ t produced experimental anode paste on 11 July and 20 July 1983 respectively. Whereas composite sample marked IV was made $99 + 65 = 165$ t anode paste produced on 21 - 22 July 1983.

Sample of experimental as well as regular anode paste calcined petroleum coke, binding material and AlF_3 has been collected and prepared for dispatch to Hungary.

Laboratory analysis reports on samples of experimental anode paste marked No. I and No. II and description or Government's laboratory analysis method would be attached for this Report. Laboratory analysis reports on samples marked No. III and No. IV will be send for BUDAPEST, for Contractor's laboratory later on.

2.2 Aluterv-FKI's Laboratory Analyses of Raw
Materials and Products of Experiments in
Balco's Anode Paste Plant

In the course of experimental anode paste production samples were taken as per Application Description for the purpose of analysis either in Contractor's or Government's laboratory. Contractor's laboratory analysis results as well as comments on them can be seen on the following pages.

It can be stated on the basis of laboratory analysis results that properties of anode paste were improved with addition of aluminium fluoride.

ALUTERV FKI'S LABORATORY ANALYSIS REPORT

Of Anode Paste with AlF_3 and Its Raw Materials
Produced At Korba, Balco's Anode Paste Plant

1) C.P. COKE		COKE GRANULATION	
Moisture	0.02 %	+10 mm ~	38.1 %
Ash content	0.38 %	5-10 mm	8.7 %
Volatile	0.38 %	1-5 mm	26.5 %
Sulfur content	0.5 %	0.5-1 mm	11.6 %
Real Density	2.077 g/cm ³	0.1-0.5 mm	14.1 %
Oil content	0.11 %	0.06-0.1 mm	0.5 %
		0.06 mm	0.5 %
2) Binding Material			
Insoluble in Anthracene oil			11.6 %
Insoluble in Benzene			33.4 %
Softening point according to K.S.			78.0°C
3) Aluminium Fluoride			
Moisture on 110°C			0.7 %
Fluorine Content			61.0 %
AlF_3 Content			89.9 %
P_2O_5			0.1 %
Na_2O			0.3 %

Study for Anode Paste

Sl. No.	Particular	Experimental Paste with AlF ₃				Normal Paste	
		July 1,6,7 1983	July 9,10 1983	July 20 1983	July 21 1983	July 18 1983	
(A) <u>Green Paste</u>							
1	Ash	%	0.66	1.16	0.71	0.63	0.23
2	Volatile Matter	%	15.9	16.4	15.7	15.3	15.5
3	Sulfur Content	%	0.46	0.49	0.47	0.51	0.55
4	Solubility in Anthracene Oil	%	28.5	31.6	28.8	28.5	29.9
5	Plasticity	%	67.0	65.0	70.0	76.0	67.0
6	Elongation Number by Stanko's method	%	149	125	208	168	183
7	AlF ₃ Content	%	0.65	0.93	0.65	0.66	Nil
8	Bulk Density	gm/cm ³	1.584	1.565	1.591	1.591	1.561

Cont.

Sl. No.	Particular	Experimental Paste with AlF ₃				Normal Paste
		July 1,6,7 1983	July 9,10 1983	July 20 1983	July 21 1983	July 18 1983

(B) Baked Paste

9	Bulk Density	g/cm ³	1.350	1.315	1.296	1.315	1.298
10	Compressive Strenth	Kg/cm ²	248	187	184	193	179
11	Specific Resistance	$\mu\Omega\text{cm}$	75	76	87	77	72
12	Caroxy Reactivity by Scalliet	mg/cm ² /h	29	26	31	27	41
13	Skim Scalliet	mg/cm ² /h	7	7	7	6	9
14	Gas Permeability	nPm	105	105	187	116	101

2.3 Balco's Laboratory Analyses of Raw Materials
and Products of Experimentens in Balco's
Anode Paste Plant

Unbroken charging of aluminium fluoride anode paste to experimental cells and regular anode paste for reference cells. However, on cell No. 347 capital repair started on 13.10.1983, and it was recommissioned on 16.11.1983. Cell No. 349 was recommissioned on 30.07.1983. Similarly cell No. 330 and 331 closed down on 30.07.1983 and 29.07.1983 and they were recommissioned on 16.09.1983 respectively. Those cells are taken out of study.

Various technological parameters were measured and recorded. On the basis of these data, tables and graphs have been made.

Several laboratory analysis were carried out on aluminium fluoride anode paste samples. Results of these analysis are shown on the next pages.

MANUFACTURING DETAILS OF ANODE PASTE WITH
ALUMINIUM FLUORIDE

Date of Manufacture	1st July 1983	6,7,9 and 10 July 1983	11,14,20, 21, 22 July 1983	
Quantity Manufactured (t)	27	372	342,6	
Coke	kg	1955	1952	1944
Bin Fine (40 %)	kg	782	779	777
-14+48 = (20 %)	kg	391	391	389
- 3+14 = (40 %)	kg	782	782	778

Cont.

Date of Manufacture		1st July 1983	6,7,9 and 10 July 1983	11,14,20, 21, 22 July 1983
Binding Material	kg	1027	1027	1035
Aluminium Fluoride	kg	18	21	21
Dry Mixing and Preheating Time	min.	20	5	5
Mixing Time During Pitch Addition	min.	5	5	5
Mixing Time Coke+AlF ₃ +Pitch	min.	40	30	30
Total Mixing Time	min.	65	40	40
Temperature of mixing.	°C	145-165	145-165	145-165

ANALYSIS REPORT
RESEARCH AND CONTROL LABORATORY

C.P. COKE FROM IOC, BARAUNI

Analysis

1) Moisture	0.035
2) Ash %	0.21
3) VM %	0.210
4) R.D. g/cm ³	2.04

Chemical Analysis

1) SiO ₂	0.04 %
2) Fe ₂ O ₃	0.05 %
3) TiO ₂	0.0008 %
4) V ₂ O ₅	0.00073 %
5) S -content	0.63 %

Cont.

Screen Analysis

+12 mm	20.0 %
+ 4.76 mm	36.5 %
+ 0.84 mm	34.50 %
+ 0.296 mm	7.0 %
- 0.296 mm	2.0 %

C.T. PITCH FROM NISSO IWAI JAPAN

Analysis

Softening Point (R and B)	94°C
Coking Value %	55.50
Ash %	0.15
Benzene Insoluble %	32.40
Quinolene Insoluble %	9.20
Beta Resin %	23.20

Distillation

Upto 300°C	0.34 %
301 - 360°C	3.35 %

ALUMINIUM FLUORIDE FROM NAVIN FLUORINE
INDIA USED FOR MAKING EXPERIMENTAL ANODE
PASTE

Analysis

1) Moisture %	0.09 %
2) LOI at 550°C for 1/2 hrs	0.31 %
3) AlF ₃ %	90.35 %
4) Al ₂ O ₃ (free)	7.90 %
5) F	61.30 %
6) Al	33.21 %

Cont.

7) SiO_2 %	0.087 %
8) Fe_2O_3 %	0.025 %
9) P_2O_5 %	0.017 %
10) SO_3 %	0.17 %
11) Na_2O %	0.10 %
12) B/D gpl	1400

BALCO LABORATORY REPORT OF SIEVE ANALYSIS OF COKE FRACTION IN
VARIOUS BINS EMPLOYED FOR MANUFACTURING ANODE PASTE WITH AlF_3
PRODUCED AT ANODE PASTE PLANT BALCO KORBA

Date of Sample	Bin	+12 mm	-12 mm	-6 mm	-4 mm	-2 mm	-1 mm	-0,15 mm	-0,07mm	-0,53
		%	+ 6 mm %	+4 mm %	+2 mm %	+1 mm %	+0,15 mm %	+0,074 mm %	+0,053 mm %	mm %
1.7.83 I	-3 +4 ≠	-	22.50	22.50	55.00	-	-	-	-	-
	-4 +14 ≠	-	-	-	25.50	67.00	7.50	-	-	-
	-14+48 ≠≠	-	-	-	16.50	64.00	19.50	-	-	-
	Ball Mill Fine	-	-	-	-	0.50	12.00	18.00	22.00	47.50
1.7.83 II	-3 +4 ≠	-	48.50	23.00	27.50	1.00	-	-	-	-
	-4 +14 ≠	-	-	-	3.00	5.00	76.00	8.50	3.00	4.50
	-14+48 ≠	-	-	-	-	-	92.50	6.50	1.00	-
	Ball Mill Fine	-	-	-	-	0.50	15.00	23.50	18.50	42.50
9.7.83	-3 +4 ≠	-	28.50	20.50	51.00	-	-	-	-	-
	-4 +14 ≠	-	-	-	42.50	52.00	5.50	-	-	-
	-14+48 ≠	-	-	-	-	-	93.50	5.50	1.00	-
	Ball Mill Fine	-	-	-	-	-	18.00	31.00	19.50	31.50

Cont.

Date of Sample	Bin	+12 mm %	-12 mm + 6 mm %	-6 mm +4 mm %	-4 mm +2 mm %	-2 mm +1 mm %	-1 mm +0,15 mm %	-0.15 mm +0,074 mm %	-0,07 mm +0,053 mm %	-0,053 mm %
10.7.83	-3 +4 ≠	-	27.50	20.00	52.50	-	-	-	-	-
	-4 +14 ≠	-	-	-	42.50	52.00	5.50	-	-	-
	-14+48 ≠	-	-	-	-	-	93.50	5.50	1.00	-
	Ball Mill Fine	-	-	-	-	-	18.00	31.00	19.50	31.50
20.7.83	-3 +4 ≠	-	46.00	17.50	36.50	-	-	-	-	-
	-4+14 ≠	-	-	-	41.50	54.00	4.50	-	-	-
	-14+48 ≠	-	-	-	-	-	91.00	6.00	3.00	-
	Ball Mill Fine	-	-	-	-	-	-	-	-	-
21 and 22	-3 +4 ≠	-	44.50	21.00	34.50	-	-	-	-	-
	-4+14 ≠	-	-	-	55.50	38.00	6.50	-	-	-
July'83	-14+48 ≠	-	-	-	-	-	89.00	8.50	2.50	-
	Ball Mill Fine	-	-	-	-	0.50	19.00	29.50	17.00	34.00

BALCO LABORATORY ANALYSIS REPORT
of Anode Paste with AlF_3 Produced at Anode
Paste Plant, BALCO, KORBA

	1, 6, 7 July 1983	9 and 10 July 1983	20 July 1983	21 and 22 July 1983
Quantity Produced (Ton)	138	261	132.6	165
(A) GREEN PASTE ANALYSIS				
Plasticity %	58.34	55.91	68.57	60.00
Fluidity Ratio (VAMI)	2.38	2.21	2.24	1.92
Ash Content %	0.70	0.85	1.05	0.76
Pitch Content %	30.96	33.03	31.02	33.59
AlF_3 Content %	0.65	0.78	0.64	0.64
(B) GRANULOMETRIC COMPOSITION				
+12 mm %	-	-	-3.77	-
-12+6 mm %	4.55	5.42	5.66	6.15
- 6+4 mm %	4.87	3.10	3.77	3.08
- 4+2 mm %	17.87	16.12	14.16	15.38
- 2+1 mm %	15.28	15.50	11.32	17.70
- 1+0.15 mm %	24.60	24.80	24.53	36.92
- 0.15+0.074 mm %	11.70	14.26	16.04	4.62
- 0.074+0.053 mm %	9.75	11.78	9.43	10.77
- 0.053 mm %	11.38	9.02	1.32	5.38
(C) BAKING TEST				
Bulk Density gm/cm ³	1.33	1.39	1.31	1.32
True Density gm/cm ³	2.03	2.03	2.04	2.04
Porosity %	34.48	31.5	35.7	35.2
Cold Crushing Strength Kg/cm ²	228	285	142	152
Resistivity ohm/mm ² /m	50	40	50	50
AlF_3 Content %	0.74	1.00	0.67	0.67

METHODS OF ANALYSIS

I - PLASTICITY

Module \varnothing 60 mm
 h 70 mm

Load 0.187 Kg/cm²
 Temp. 100°C

Boil the module in Hot water for 10-15 minutes, apply load in boiling water for 30 minutes.

$$\text{Plasticity} = \frac{\text{Difference in height}}{I.D (70)}$$

II - FLUIDITY RATIO

Module \varnothing 50 mm
 h 50 mm

Air Oven heat 170°C for 30 minutes.

$$\text{Fluidity Ratio} = \frac{\text{Average Final Diameter}}{\text{Initial Diameter (50 mm)}}$$

2.4 Second Phase of Experiment: - Observation
before Experimental Paste Entering Reaction
Zone

Quality of anode paste being applied by KORBA Aluminium Smelter shows substantial difference from that quality of anode paste on which skim-reducing effect of AlF_3 additive was verified. We agreed that we would prove the skim-reducing effect of AlF_3 in case of application of this anode paste further we would cooperate in development of composition of high softening point anode paste with AlF_3 additive.

We perform the tasks of first phase of experimental period as the required quantity of experimental anode paste has been produced. Tasks of analysis of samples will be done by contractor.

We agreed that technological measurements as fixed up in the programme as well as the separated skim-collection would be done by Government's Personnel on experimental and reference cells from 01 August 1983 for the end of experimental period.

Experimental anode paste samples will be taken by Government's Personnel from anode top of experimental cells once weekly for analysis of AlF_3 content.

Laboratory analysis reports on experimental anode paste marked I and II show improvement in properties of anode paste comparing the same to regular anode paste properties respectively.

For application and inspection to be done while applying aluminium fluoride anode paste it was suggested to Government's Personnel to take advantage of Contractor's laboratory experiments and send their experts to

BUDAPEST for training in laboratory analysis methods and smelting technology. It would help in solution of existing anode paste problems and in transferring know how.

Contractor's Personnel state that Government's Personnel did their best in spite of their difficulties for the interest of successful implementation of experimental programme.

2.5 Third Phase of Experiment: - Observation
and Evaluation after Experimental Paste
Entering Reaction Zone

Parties determined the target of technological experiment in improvement of presently produced anode paste with addition of inorganic AlF_3 additive. Skim-decreasing effect of AlF_3 additive was examined on the following way. Technological parameters measured on experimental cells were compared to parameters of reference cells. For this comparison cells nearly with the same age were selected.

Technological parameters were measured and recorded by Government representatives on the basis of programme enclosed herewith.

The following table shows the technological parameters either for experimental or reference cells.

The most important technological parameters are figured in the function of time like;

- current efficiency, metal production (Fig. 1)
- Skim-generation, anode paste consumption
(Fig. 2)
- Silicon content in metal (Fig. 3)
- Energy consumption (Fig. 4)
- Aluminium fluoride consumption (Fig. 5)

Relationship between current efficiency and metal production is favourably evident from the diagrams. It can be stated that there is improvement in current efficiency on experimental cells from middle of September as the skim started to decrease. It is because the anode paste flows into holes during stud change.

In initial stage current efficiency of reference cells were higher but by the end of experimental period the current efficiency of experimental cells became higher. Remarkable decrease in specific anode consumption can be observed. Quantity of skim apparently increased but in comparison to reference cells the skim decreasing effect of aluminium fluoride can be seen.

The quantity of skim increased due to lasting power failure. Lesser skim generation as compared to reference cells was caused probably by higher compactibility of anode paste containing AlF_3 .

In harmony with current efficiency - time and anode paste consumption - time diagrams, decreasing of Silicon content in metal can be observed from middle of September whereas in the reference cells the Silicon content was always higher.

Decreasing of AlF_3 consumption is caused by utilization of aluminium fluoride anode paste too.

In consequence of lower skim quantity and frequency of skimming, the quantity of removed electrolyte from bath is less.

Power consumption in experimental cells was lower than in reference cells and it remained lower by the end of experimental period, too.

In general it can be observed from diagrams that the effect of AlF_3 additive is more perceptible from middle of September as more fluid anode paste has flown into the holes during stud change.

Reduction in skim generation is more than 15 % as cold running technology ensures better separation of skim and electrolyte, therefore efficiency of skimming is higher.

From lower current efficiency of reference cells it is possible to conclude that hot running technology is prevailing leading to increased carbon content of electrolyte and lower quantity of skim can be removed.

Table 2.1
COMPARATIVE STATEMENT OF PERFORMANCE
WITH ANODE PASTE CONTAINING ALUMINIUM FLUORIDE

		1 Aug - 21 Oct 1983		22 Oct - 20 Nov 1983	
		Before Experi- mental Paste entered the Reaction Zone		After Experi- mental Paste entered the Reaction Zone	
Duration of Study (Days)		82		30	
Average Line Current		kA 94.162		94.325	
Item	Unit	Normal Group	Exp'tl Group	Normal Group	Exp'tl Group
Mean Potencial	V	4.4207	4.4122	4.4308	4.4533
Basic Potencial	V	4.20	4.20	4.2021	4.2204
Specific Energy	kWh/t	15982	17111	15861	15241
Metal Production	kg/cell	625.039	582.713	632.348	661.433
Current Effi- ciency	%	82.47	76.88	83.29	87.12
Anode Mass	kg/t	531.311	562.984	550.726	526.296
Removed Scum	kg/t	53.56	41.39	57.09	49.63
Effect No.	No/Cell Day	1.95	1.71	2.02	1.85
AlF ₃ Consump- tion	kg/t	50.19	55.56	50.56	44.85
Si Content in Metal	%	0.1405	0.1073	0.0862	0.0693
Energy Effi- ciency	%	41.6	39.6	41.81	43.09

IMPROVEMENT IN CURRENT EFFICIENCY AND METAL PRODUCTION WITH PASTE CONTAINING AlF_3

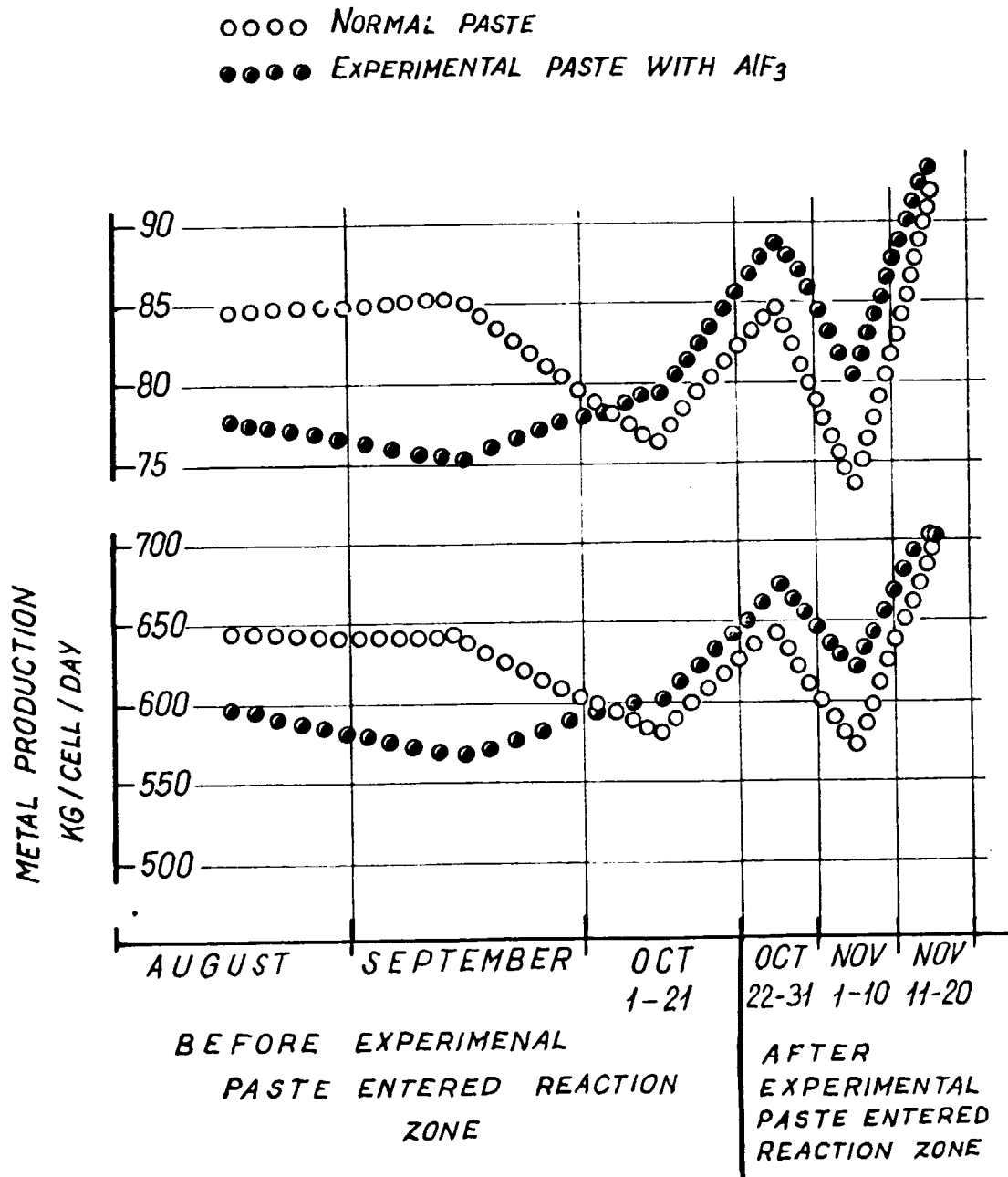


Fig. 1.

REDUCTION IN SKIMMING GENERATION AND ANODE MASS CONSUMPTION WITH PASTE CONTAINING AlF_3

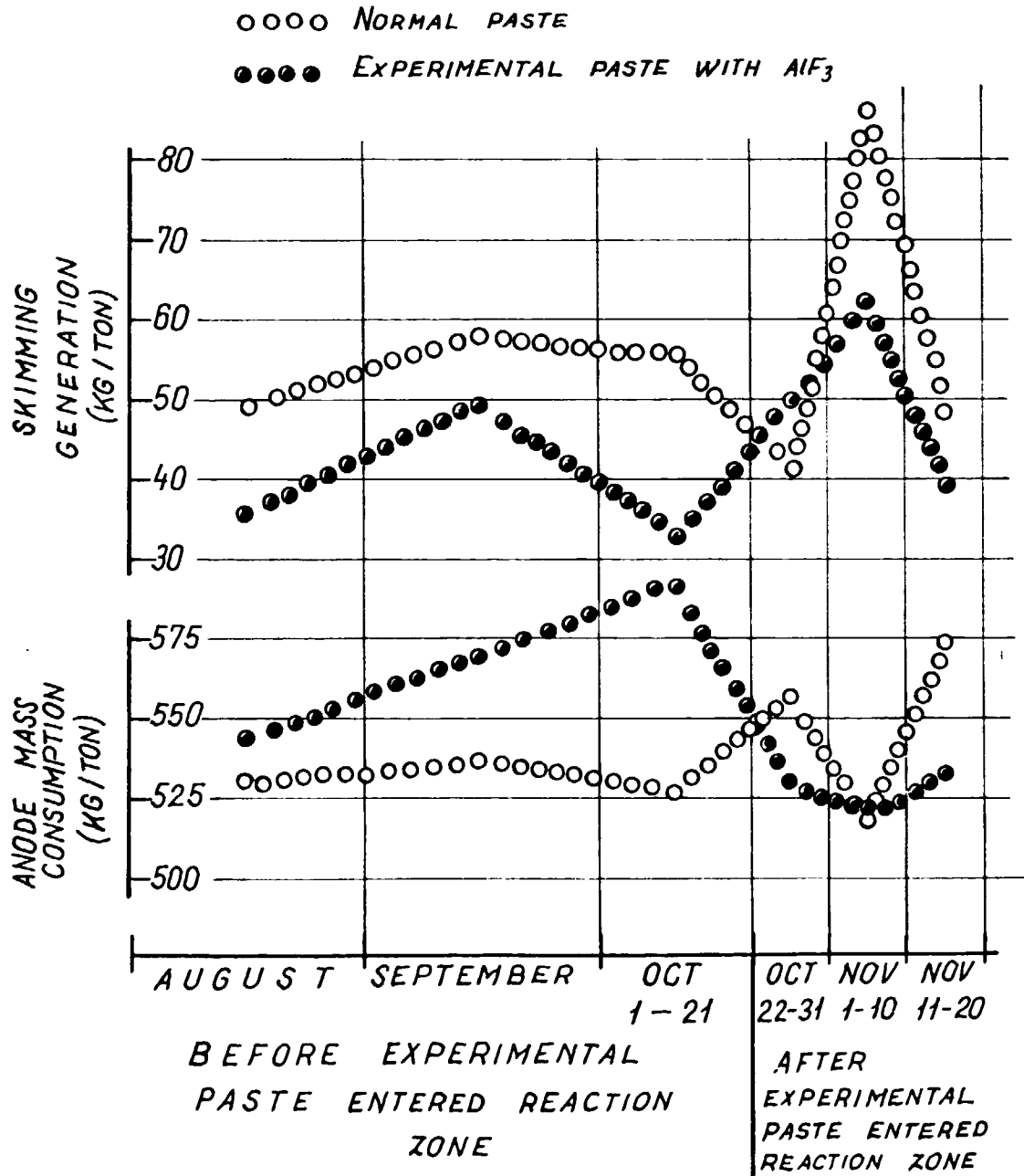


Fig. 2

REDUCTION IN SILICON CONTENT IN CELL METAL WITH ANODE PASTE CONTAINING AlF_3

○ ○ ○ ○ NORMAL PASTE
● ● ● ● EXPERIMENTAL PASTE WITH AlF_3

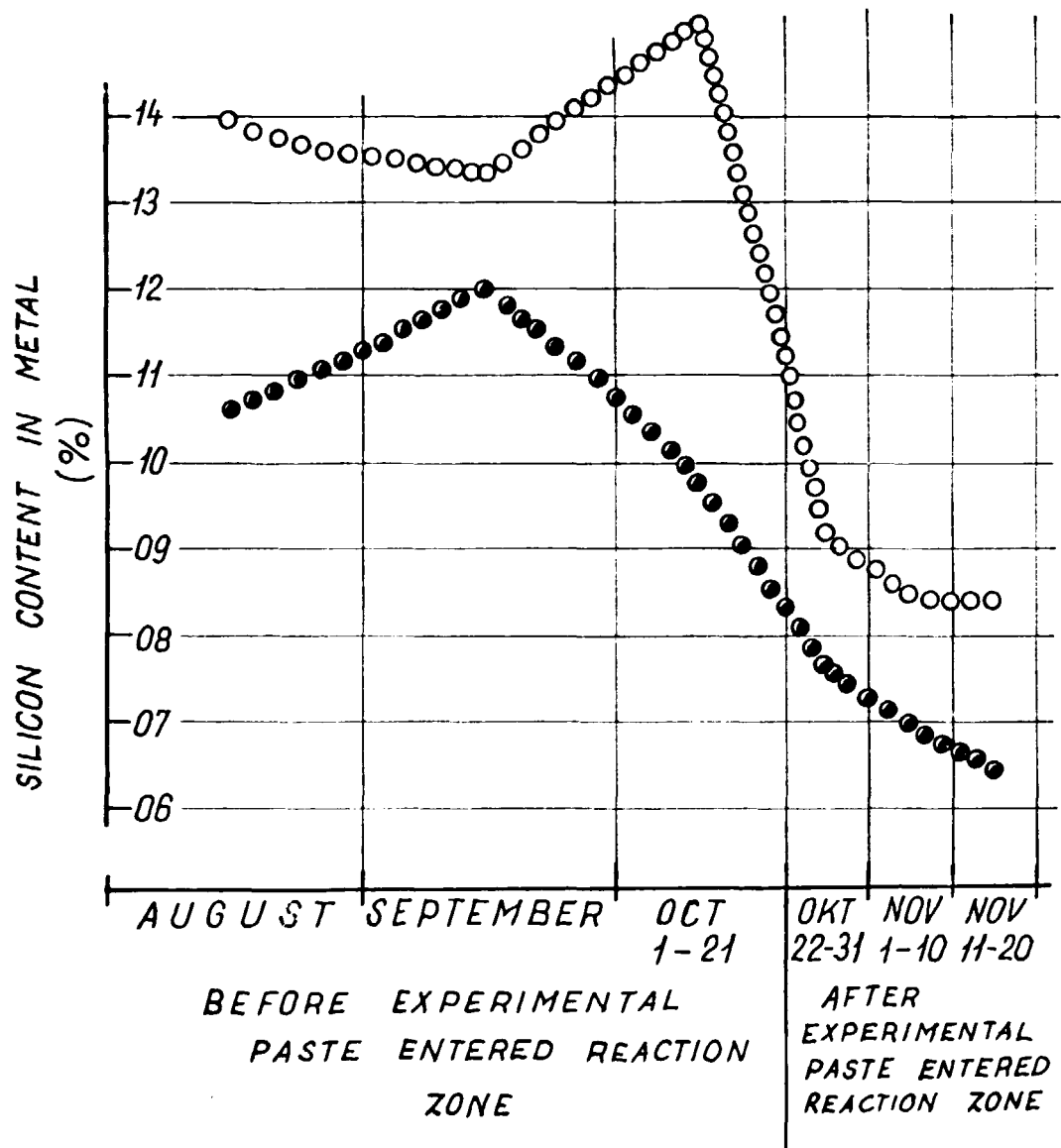


Fig. 3

REDUCTION IN POWER CONSUMPTION
WITH ANODE PASTE CONTAINING AlF_3

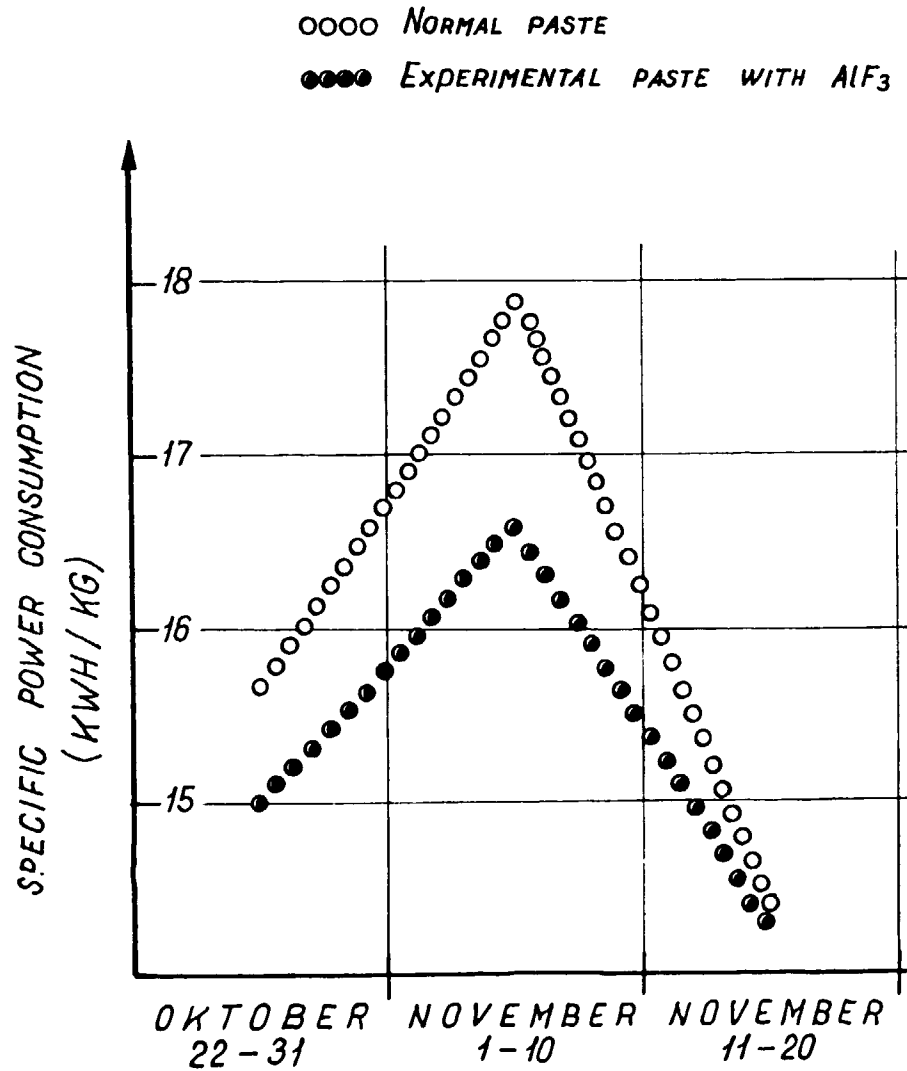


Fig. 4

IMPROVEMENT IN CONSUMPTION OF ALUMINIUM FLUORIDE WITH ANODE PASTE CONTAINING AlF_3

○ ○ ○ ○ NORMAL PASTE
● ● ● ● EXPERIMENTAL PASTE WITH AlF_3

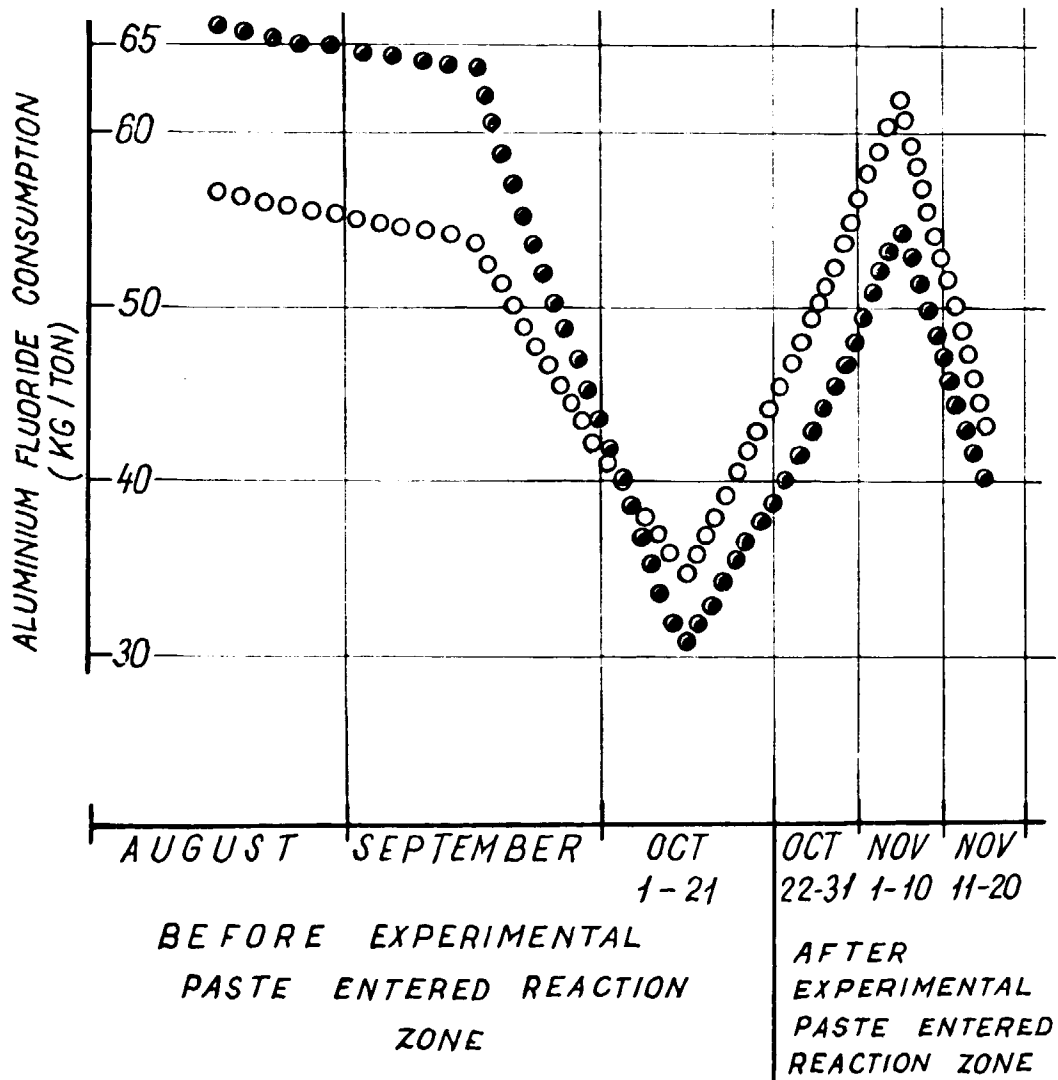


Fig. 5

2.5.1 Supplement of the Report

In the "Summary and Recommendations" Chapter of Draft Final Report dated 29 November 1983 the parties established that the anode mass with AlF_3 additive had favourable effect on the technological parameters, during shortterm experiments.

The results in Draft Final Report have been supplemented with results of an additional 2-month experiment. These additional results have been determined by the plant in the way defined by the program. These results are shown in the table 2.2 and the Fig. 6 - 12.

The presently about 3-month long experimental period is deemed to be suitable to prove unequivocally the favourable effect of AlF_3 containing anode mass. At the same time this long duration minimises possibility of any effect of fluctuations in technology to the results, and ensures the reproducibility of the results. The results are summarised in table 2.3.

Table 2.2

PERFORMANCE WITH ANODE PASTE CONTAINING ALUMINIUM
FLUORIDE DURING THE ADDITIONAL TWO MONTHS' EXPERI-
MENT 21.11.83-19.1.84

Average Line Current		kA	95.687	
Item	Unit	Normal Group	Experimental Group	
Mean Potential	V	4.3992	4.4253	
Basic Potential	V	4.2152	4.2171	
Specific Energy	kWh/t	15851	15671	
Metal Production	kg/cell/day	638.214	649.225	
Current Efficiency	%	82.86	84.29	
Anode Mass	kg/t	588	551	
Removed Scum	kg/t	68.71	58.07	
Effect Number	No/cell/day	1.52	1.81	
AlF ₃ Consumption	kg/t	44.52	48.00	
Si Content in Metal	%	0.0985	0,0750	
Energy Efficiency	%	41.86	42.16	

Table 2.3

COMPARATIVE STATEMENT OF PERFORMANCE
WITH ANODE PASTE CONTAINING ALUMINIUM FLUORIDE

		1 Aug - 21 Oct 1983		22 Oct - 19 Jan 1984	
		Before Experi- mental Paste entered the Reaction Zone		After Experi- mental Paste entered the Reaction Zone	
Duration of Study	Days	82		90	
Average Line Current	kA	94.162		95.233	
Iten	Unit	Normal Group	Exp'tl Group	Normal Group	Exp'tl Group
Mean Potential	V	4.4207	4.4122	4.4080	4.4346
Basic Potential	V	4.20	4.20	4.2112	4.2185
Specific Energy	kWh/t	15982	17111	15835	15204
Metal Production	kg/cell day	625.039	582.713	636.198	653.294
Current Effi- ciency	%	82.47	76.88	82.99	85.23
Anode Mass Removed Scum	kg/t	531.311	562.984	575	543
Effect No.	No/cell day	53.56	41.39	64.74	55.22
		1.95	1.71	1.68	1.85
AlF ₃ Consump- tion	kg/t	1.95	1.71	1.68	1.85
Silica Content in Metal	%	50.19	55.56	46.58	46.94
Energy Effi- ciency	%	0.1405	0.1073	0.0944	0.0731
		41.6	39.6	41.89	43.33

CURRENT EFFICIENCY

oooo NORMAL PASTE
●●●● EXPERIMENTAL PASTE

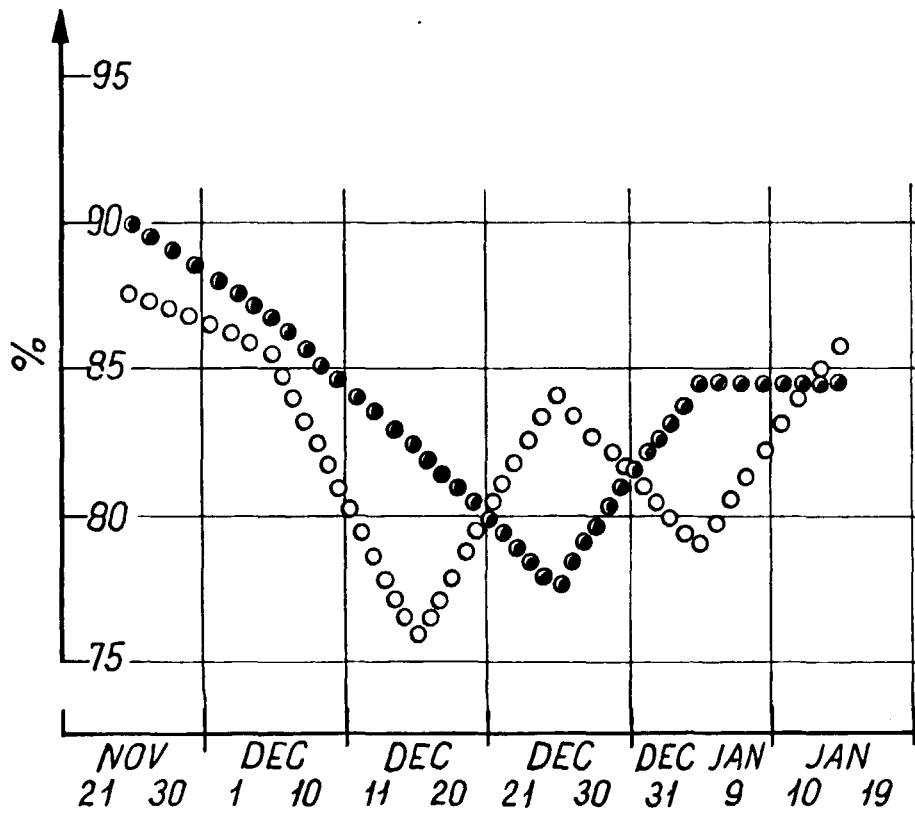


Fig.6

SKIMMING GENERATION

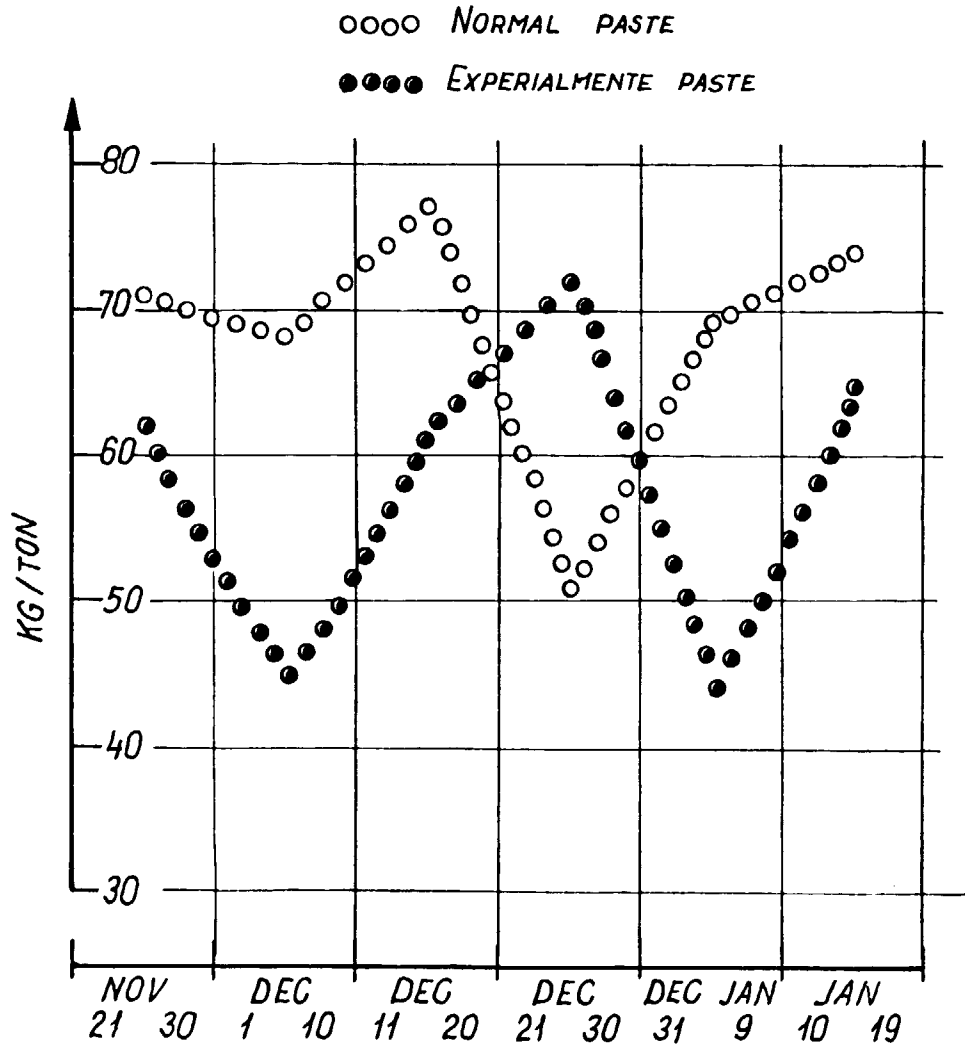


Fig. 7

METAL PRODUCTION PER CELLDAY

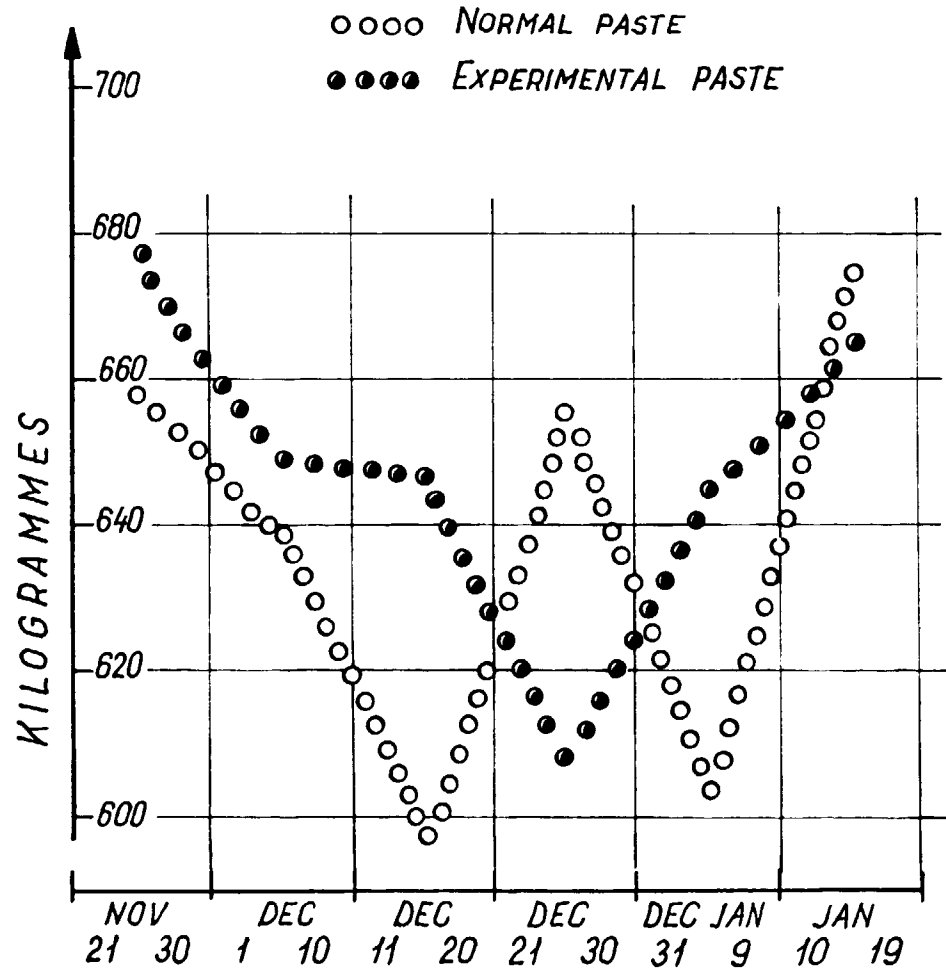


Fig. 8

AlF_3 CONSUMPTION

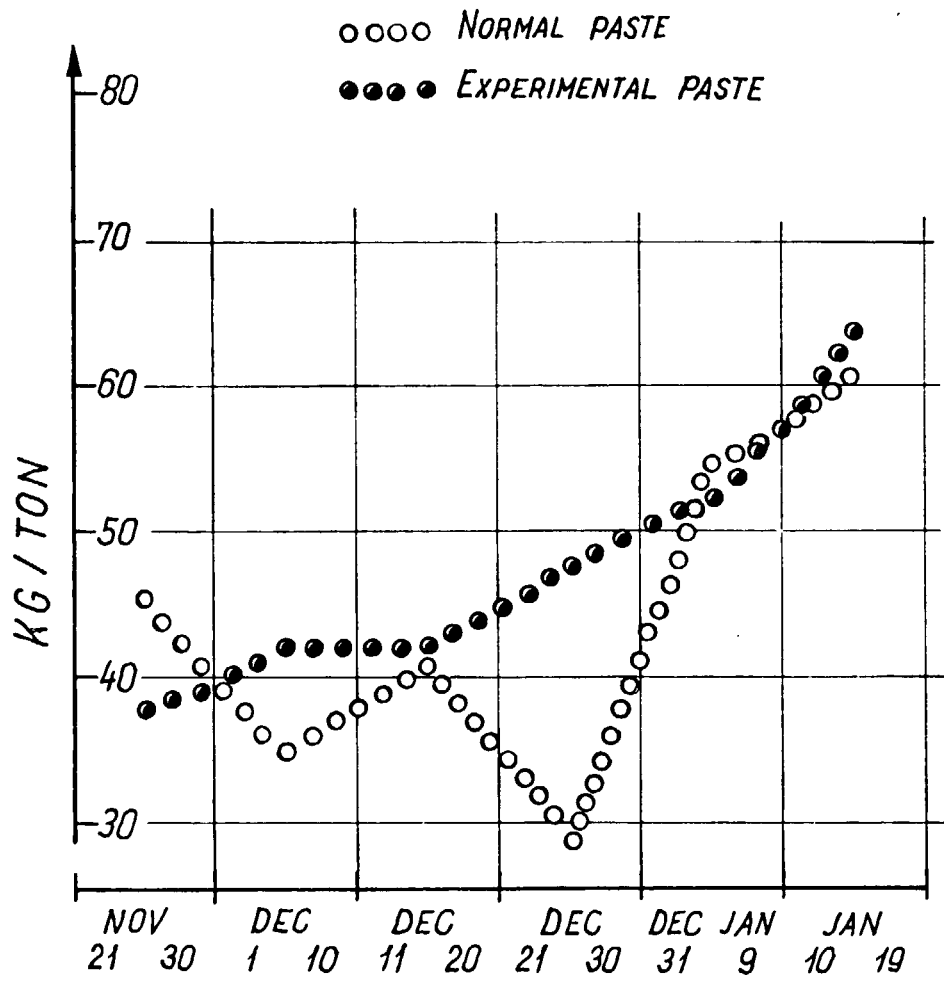


Fig. 9

ANODE MASS CONSUMPTION

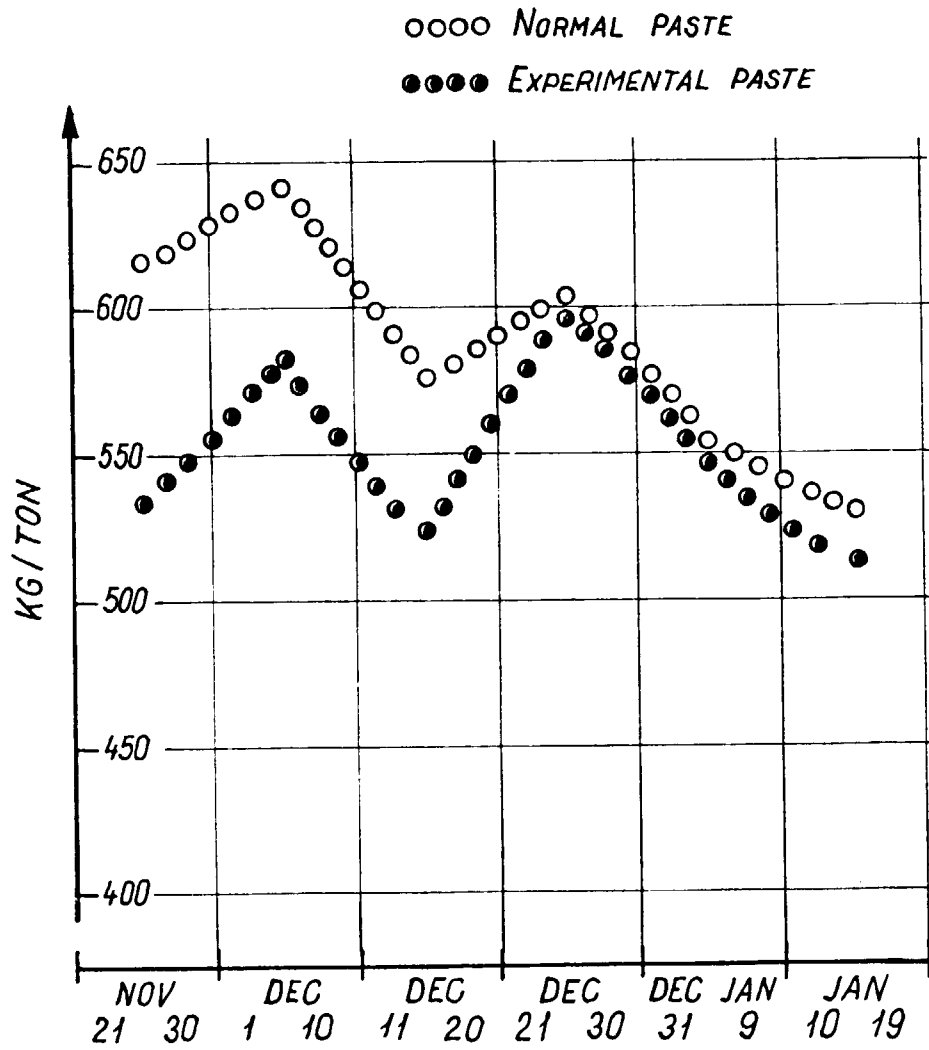


Fig. 10

SPECIFIC POWER CONSUMPTION

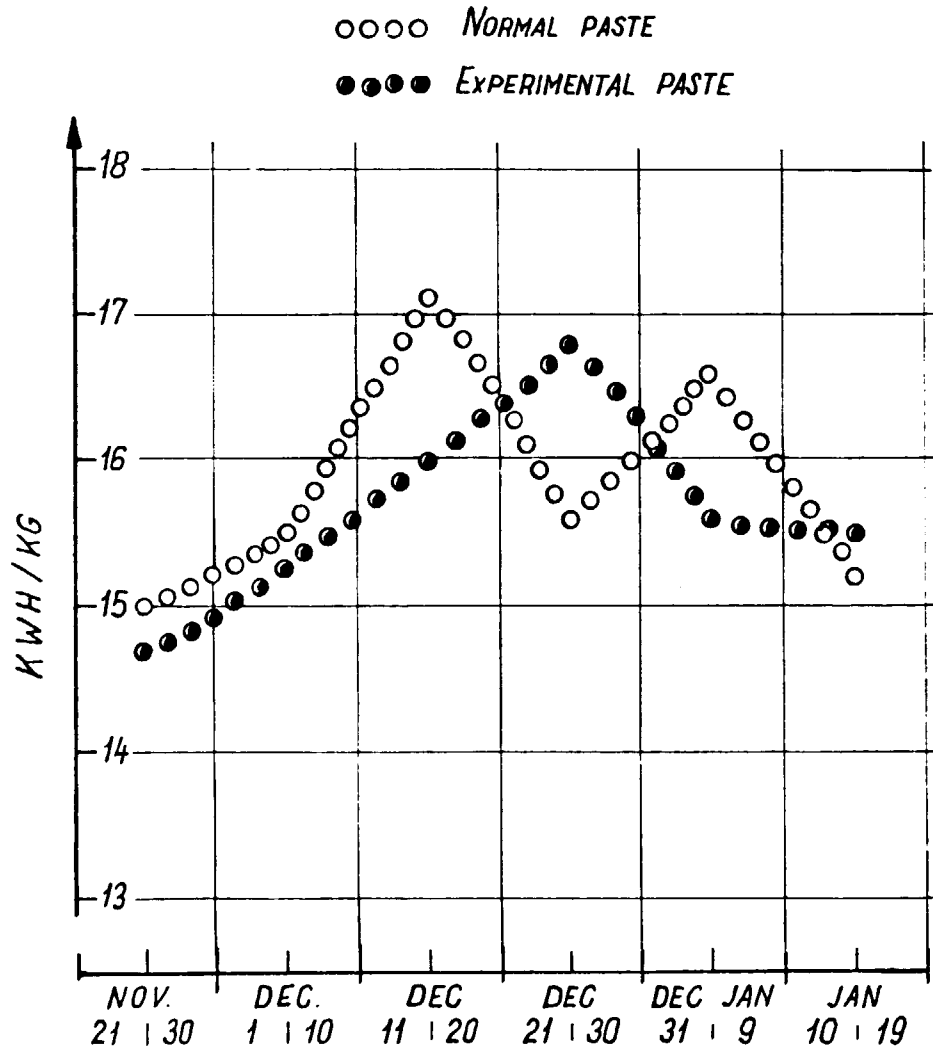


Fig.11

SILICON CONTENT IN METAL

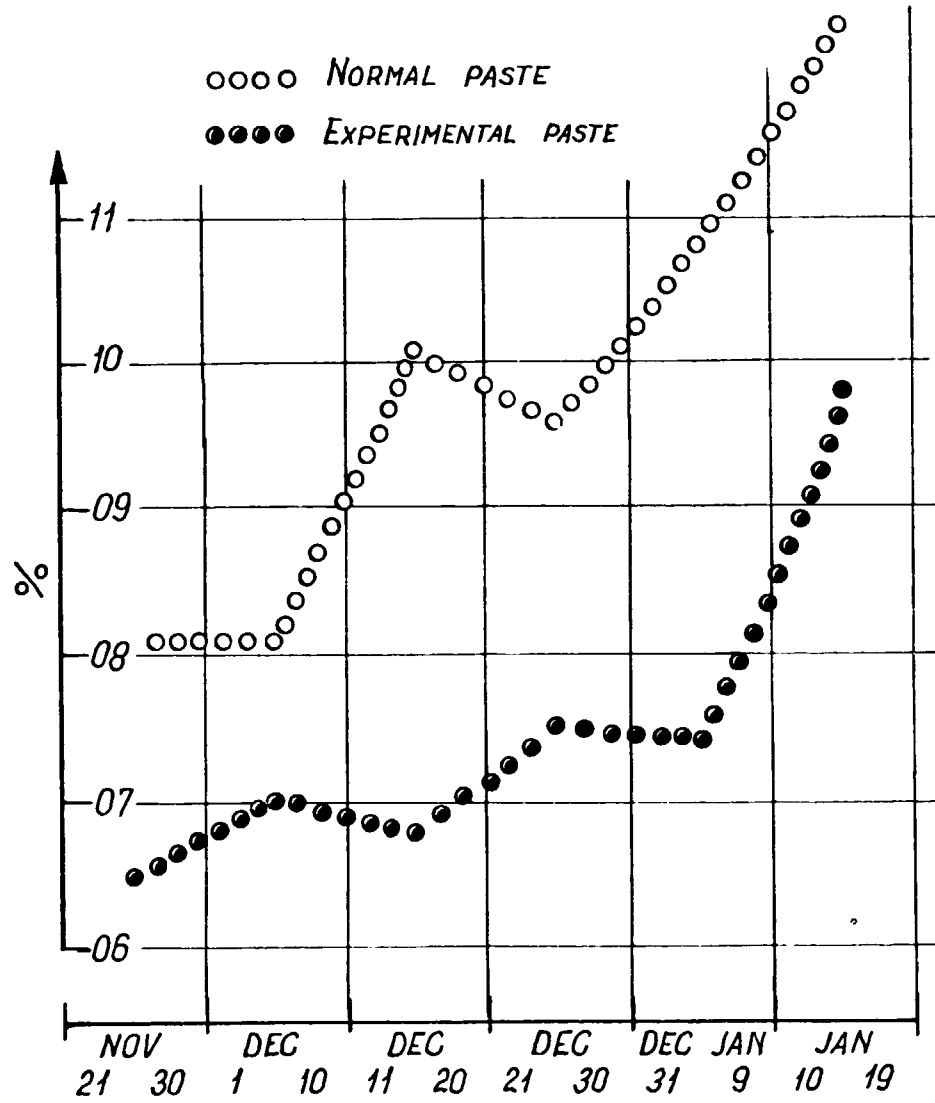


Fig.12

3. SUMMARY AND RECOMMENDATIONS

3. SUMMARY AND RECOMMENDATIONS

Results of laboratory analysis carried out either in ALUTERV'S or in BALCO'S laboratory proved that anode paste with 0.6 % AlF_3 additive had better properties than the anode paste produced with the same technology but without AlF_3 additive.

It may be stated on the basis of short duration of experiment that the application of aluminium fluoride anode paste had a favourable effect on techno-economic parameters of aluminium electrolysis.

The summarized results of utilization of aluminium fluoride anode paste as well as anode paste produced without aluminium fluoride additive are given below.

Results obtained in the course of experiment proved that use of anode paste with AlF_3 additive improves the techno-economic parameters of aluminium electrolysis. The skimming decreases by 15 % which results in decrease of heat losses at uncharged cell voltage, due to this the current efficiency is higher, the current consumption is lower. In the experimental cells the metal production increased by 4.6 %, the specific anode consumption decreased by 23.8 kg/t, the current efficiency increased by 3.83 % and the specific energy consumption decreased by 620 kWh/t in comparison to reference cells.

It is to be stated that we could realize 15 % decrease in skimming instead of 50 % having been forecast, due to different properties of anode paste being used by BALCO which differs from the one used by ALUTERV-FKI and also envisaged for this study. However, we could achieve higher current efficiency and electric power savings at the same time.

It is also important result that the AlF_3 consumption decreased with 5.71 kg/t and the Silicon content in the metal reduced to considerable extent.

It can be stated that there are differences between ALUTERV'S and BALCO'S laboratory results, may be due to different testing methods for analysis. Further, BALCO does not have adequate testing facility for determination of skim generating characteristics viz. Carboxy Activity Test.

Contractor suggests to accept the know-how of aluminium fluoride paste based on present test results.

BALCO is of the opinion that in view of short period of experiment, when at times even the other normal cells perform exceedingly well, this experiment be conducted for another two months before arriving at a final decision about the effect of AlF_3 paste. The results cover the improving effect of AlF_3 paste. For the numerical determination of improvement in techno-economic parameters due to AlF_3 paste, more data on longer experimental period is considered necessary so that the effect of fluctuations of cell technology is eliminated. The situation of power outages to cell line was not envisaged in Project Document/Assignment. In view of this, Contractor agrees for continuation of the experiment on existing experimental cells as proposed by BALCO for another two months for confirming/arriving at the test results. The preparation of anode paste with AlF_3 shall be according to the formula adopted earlier i.e. 20-22 July, 1983 for which no assistance of the Contractor is envisaged.

It is necessary that AlF_3 anode paste experiment be conducted on a larger scale, say in half a cell line for a period not less than six months for its commercial adoption.

Further the application of the process will be seen also by Balco Engineer during their training abroad as covered under the project proposal.

Contractor, in accordance with the Draft Final Report, suggests that decision should be made about adopting this know how.

On the basis of the contract between UNIDO and ALUTERV-FKI, we are hereby confirming the favourable characteristics of the anode mass with AlF_3 dope anode paste in industrial scale test in Korba Plant.

In light of the above it is suggested that the plant should perform further experiments with anode mass containing AlF_3 on a larger scale, say in half a cell line.

According to the Memorandum of Understanding between BALCO and UNIDO, necessary steps should be initiated for commercial scale adoption of the technology.

4. BIBLIOGRAPHY

4. BIBLIOGRAPHY

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Annexure A.

PROGRAMME FOR PROJECT ON IMPROVEMENT OF ANODE
PERFORMANCE WITH ADDITION OF ALUMINIUM FLUORIDE
ANODE PASTE

Programme for Production of Paste and
Carrying out the Experiment

I. (1) The experiment with aluminium fluoride anode paste will be carried out on 13 pots (one section) as measurements can be done separately on them.

The experiment starts with preparation of the fluoride anode paste.

The total quantity of fluoride anode paste to be prepared: 720 t.

It was calculated on the following way:

- specific anode paste requirement 0.58 t/t aluminium
- kg aluminium net per cell day 0.67 t
- anode paste requirement 0,3886 t/cell day
- anode paste requirement for 13 pots. 5.052 t/day

The total anode paste quantity is to be prepared within four weeks period with 180 t/week production.

The prepared aluminium fluoride anode paste should be stored in a well separated indoor place.

(2) Composition of one batch (3000 kg) experimental anode paste:

coke	1955 kg
pitch	1027 kg (34.25 %)
AlF ₃	18 kg
Total	<u>3000 kg</u>

Grain composition of coke and binding contents will not be changed. 240 (= 720/3) batches of anode paste is to be prepared.

Total aluminium fluoride -(240 x 18)
(AlF₃) (90 %) requirement=4320 kgs.

(3) Time Schedule for implementation of programme:

(a) 1st Week - 27.06.83 to 03.07.83

- Fixing up the detail programme points.
- Arrangement in Anode Paste Preparation Plant for preparation aluminium fluoride anode paste
- Preparation of the first portion (180 t) of aluminium fluoride anode paste

(b) 2nd Week - 04.07.83 to 10.07.83

04.07-1983 Starting the charging of aluminium fluoride anode paste to the following No. of Pots: 340-351 in Cell House No. 3
Preparation of the second portion of aluminium fluoride anode paste (180 t).

(c) 3rd Week - 11.07.83 to 17.07.83

- Continuous charging of aluminium fluoride anode paste to all the 13 No. of Pots.
- Preparation of the third portion of aluminium fluoride anode paste (180 t).

(d) 4th Week - 18.07.83 to 24.07.83

- Continuous charging of aluminium fluoride anode paste to all the 13 No. of Pots.
- Preparation of the fourth portion of aluminium fluoride anode paste (180 t).

(e) 5th - 16th Weeks - 25.07.83 to 16.10.83

- Continuous charging of aluminium fluoride anode paste to all the 13 Pots.

(f) 17th - 22nd Weeks - 17.10.83 to 27.11.83

- Continuous charging of aluminium fluoride anode paste till the end of 142 days experimental period
- Controlling and measuring of the various technology parameters as per point-III of this programme
- Laboratory tests as per point-II of this programme
- Evaluation of the result of anode paste experiment.

(4) Selection of Cells for anode paste experiment:

It was agreed between BALCO and UNIDO Expert that Cell No. 340 to 351 in Cell House No. 3 would be selected for aluminium fluoride anode paste experiment.

The reference cells for comparison of the measured technical parameters will be Cell No. 327-339 in Cell House No. 3.

II. SAMPLING AND ANALYSIS

Following measurements are to be conducted:

- coke granulation (daily four times);
- softening point of used binding material to R and B (daily four times);
- coking residue (daily four times) to as per written description applicable;
- determination of the fluidity ratio from produced anode paste, collected average sample (during four hours period);
- from 4 hours average sample of produced anode paste, determination of ash content insolubility in benzene, aluminium fluoride content;
- from average sample of all the 180 t of produced anode paste baking and examination of laboratory specimen (5 kg samples for Aluterv-FKI measuring);
- solubility in anthracene oil;
- ash content;
- AlF_3 content;
- fluidity ratio;
- grain composition of coke without binding material real density.
Baked laboratory specimen:
 - specific resistance
 - carboxy reactivity (in Co_2 $T=950^\circ$ by Scalliet) to be done at Aluterv-FKI
 - compressive strength
 - real density

- porosity
- AlF_3 content
as per details given in "Application Description".

One portion (180 t) of experimental anode paste will be produced during 15 hours.

The samples of raw material (coke and pitch) and ready paste should be collected from each batch and a 4 hrly composite sample be made from such collected samples.

III. PERFORMANCE PARAMETERS

The following parameters are to be measured during technological experiment. On experimental and reference cells.

- Mean cell voltage
- Basic cell voltage
- Anode effect (every day)
- Anode consumption (every day)
- Energy consumption (every day)
- Metal level (every day)
- Tapped liquid metal
- Anode voltage drop (every week in three point)
- Cathode voltage drop (every week)
- Temperature of anode top (every week)
- Electrical resistivity of bath (every week)
- Bath temperature (every week)
- Removed scum quantity and frequency
- Carbon content of scum (in every portion)

- Si content in metal (at every tapping)
- Current efficiency with Cu-Al alloys application (beginning and the end of measurement)
- Height of anode level (every week)
- Distribution of currents in anode stud (every week)
- AlF_3 and cryolite consumption (every week)

Annexure B.

SI/IND/82/801 - IMPROVEMENT OF ANODE PERFORMANCE
IN ALUMINIUM SMELTING

A meeting to review the above project was held in UNDP Office, New Delhi at 1530 hrs. on 29 November 1983. The following participated in this meeting:

GOVERNMENT OF INDIA

- Mr. C.P.S. Nair
Adviser (S and T)
Department of Mines
Ministry of Steel and Mines, New Delhi

BHARAT ALUMINIUM COMPANY LIMITED

- Mr. S. S. Nandi
Deputy General Manager (P)
- Mr. I. K. Agrawal
Chief Technologist
- Mr. P. N. Sharma
National Project Coordinator
- Mr. G. D. Upadhyay
- Mr. P. K. Gairola
Assistant Superintendent (Smelter)

UNIDO SUB-CONTRACTOR PERSONNEL

- Dr. F. Horvath (Team Leader)
- Mr. T. Ferenczi

UNIDO

- Dr. M. Kamal Hussein
Senior Industrial Development Field Adviser,
New Delhi

UNDP

- Mr. Tilak R. Maakan
Senior Programme Officer

The Draft Final Report and the approved project document were used as reference material.

The 'Summary and Recommendations' of the Draft Terminal Report (attached) were discussed and accepted.

It was agreed that:

- (i) BALCO will continue experiment on existing experimental cells, as demonstrated by the Contractor, for another two months through 31 January 1984 for confirming/arriving at new test results.
- (ii) The results of such experiments will be intimated to UNDP, New Delhi and through them to UNIDO and the sub-contractor by the middle of February 1984.
- (iii) Depending on the positive results of the 2-month experiments, AlF_3 paste experiment will be conducted by BALCO on a larger scale, say in half a cell line, for a minimum period of six months before a decision is taken for commercial adoption.
- (iv) The larger scale experiment will be completed by 31 July 1984 and final results will be intimated by BALCO to UNDP/UNIDO and the sub-contractor by

the middle of August 1984.

- (v) The 2-week training each for Messrs. M.C. Gupta and P.K. Gairola of BALCO will be arranged by the sub-contractor in their country in February 1984.
- (vi) The training should be undertaken in February 1984. after the results of the 2-month experiments are known so that the BALCO engineers could interact with the sub-contractor during the former's training in Hungary.
- (vii) The sub-contractor will confirm to UNDP, New Delhi and UNIDO, Vienna by 15 December 1983 that the proposed training of 2 BALCO engineers will be possible in February 1984.
- (viii) The sub-contractor will submit to UNIDO before 31 December 1983 appropriate number of copies of the Draft Final Report (as outlined in Contract No. 83/6) to UNIDO for comments/approval prior to the official submission of the Final Report to the Government of India.

Mr. Nair thanked the sub-contractor's team for very good work done by them and the excellent co-operation received in the execution of similar other projects.

Dr. Horvath highly appreciated the assistance and co-operation extended by UNDP and the Government of India the successful completion of their assigned task in India.

Annexure C.

COMMENTS ON DRAFT FINAL REPORT OF IMPROVEMENT
OF ANODE PERFORMANCE IN ALUMINIUM SMELTING
IN INDIA

The application of fluoride additive in the anode paste is a Hungarian patent. By courtesy of ALUTERV-FKI, this technology was introduced in some industrial, experimental cells. This report is to sum up the results of application of fluoride additive to the anode paste of the experimental aluminium electrolytic cells in Korba plant.

During the first phase (from 23.6.1983 to 31.7.1983) of experiment a total of 720 tons of fluoride anode was prepared in the presence of contractor's personnel and began to be charged to selected cells on 4.7.1983. During the second phase (from 1.8.1983 to 16.10.1983) the Government's personnel at project area charged the experimental anode paste into selected experimental cells and recorded all the determined parameters of experimental and reference cells.

During the third phase (from 17.10.1983 to 27.11.1983) of experiment Government and contractor's personnels measured and evaluated the effects of fluoride additive in the anode paste on the experimental cells.

The following improvement of technical economic parameters of aluminium electrolysis has been obtained during the above experiments as compared with the reference cells:

decrease of skimming	15 %
increase of current efficiency	3,83 %
increase of metal production	4,6 %

decrease of specific energy consumption	620 kWh/t
decrease of specific anode consumption	23,8 kg/t

The report offers us excellent results of the experiments made by contractor's personnels and the counterpart's personnels in Korba, which are very encouraging in further improving the present operation of electrolytic cells.

Since the quality of anode paste in Korba showed substantial difference from that of subcontractor as claimed, but it still obtains excellent results in the experimental cells. It seems that the skim-reducing effect is not the chief effect of the fluoride additive, which showed only 15 % decrease instead of 50 %.

The results of high current efficiency and electric power saving are noticeable and worth further discussing. In case the improvement of electric conductance is the result of fluoride additive, it will be adviceable to measure the conductance of the anode before and after the additive to get the first-hand materials. Having collected the necessary data, the energy saving could be calculated from the decrease of electric resistance in the cells.

An extension of two months experiment is a good consideration which is worth UNIDO's supporting, however, the above-mentioned point should be taken into consideration and the subcontractor should also point out the significance and condition of the technology to be introduced to other plant.

However, in preparing the Final Report the following observations should be taken into account and incorporated in the report.

- a) In preamble of the Draft Final Report it says that the report summarizes the activities of the second phase, but actually the result of the third phase (after experimental paste entered reaction zone) is also included in the summarization. In order to keep integrity I suggest that the draft final report should summarize the results of the three phases. The first phase could be preferably a separate section or chapter not as an Annexation, it may take the title "First Phase of Experiment - Preparation of Experimental Anode Paste"
- b) The submission of Draft Final Report to UNIDO and the discussion in Tripartite Review Meeting should not be included in the third phase of the experiment as is written on second page of Report on First Phase. Since the Draft Final Report is the result of summarizing the experimental work, it is not substantially an experiment. The date of Tripartite Review Meeting will be fixed later after having received the Draft Final Report in UNIDO.
- c) Similarly, the contractor's homework to prepare a Final Report should not be deemed as the fourth phase of experimental period.
- d) The Table of Contents should give titles to each section and annexure. Similarly a List of Tables should also be enclosed.
- e) The results of the extension of two months experiment should also be summarized and discussed as a supplement of the report.

- f) In the Summary and Recommendation, it should be mentioned that the experiment was made on what type of aluminium electrolytic cells in India and whether this kind of additive to the anode paste can be used for cells with different kind of studs.
- g) On page 3 of First Phase Report the pitch content of regular paste used by Government is 34,25. This is not understandable. It needs explanation.
- h) The title of Section I contractor's Home Office Services should be changed to "ALUTERV-FIK's Laboratory Analysis of Raw Materials and Products of Experiments in Balco's Anode Paste Plant"
- i) The title 4 of Section I should be changed to Experimental and Normal Anode Paste.
- j) The title of Section II Governmental Representatives' Activities during Second Phase of Project should be changed to "Second Phase of Experiment - Observation before Experimental Paste Entering Reaction Zone"
- k) Similarly the title of Section III Technological Experiment with AlF_3 Additive and Evaluation of Observed Data should be changed to "Third Phase of Experiment - Observation and Evaluation after Experimental Paste Entering Reaction Zone"
- l) Suggest that the contractor's Report be written according to "Basic Principles of Scientific Report Writing".

In general the report gives us very interesting and new information far beyond the original consideration. The results of experiment are excellent. All aspects and activities as indicated in the Terms of Reference have been covered with detailed description, however, the report in its present form needs further elaboration.

