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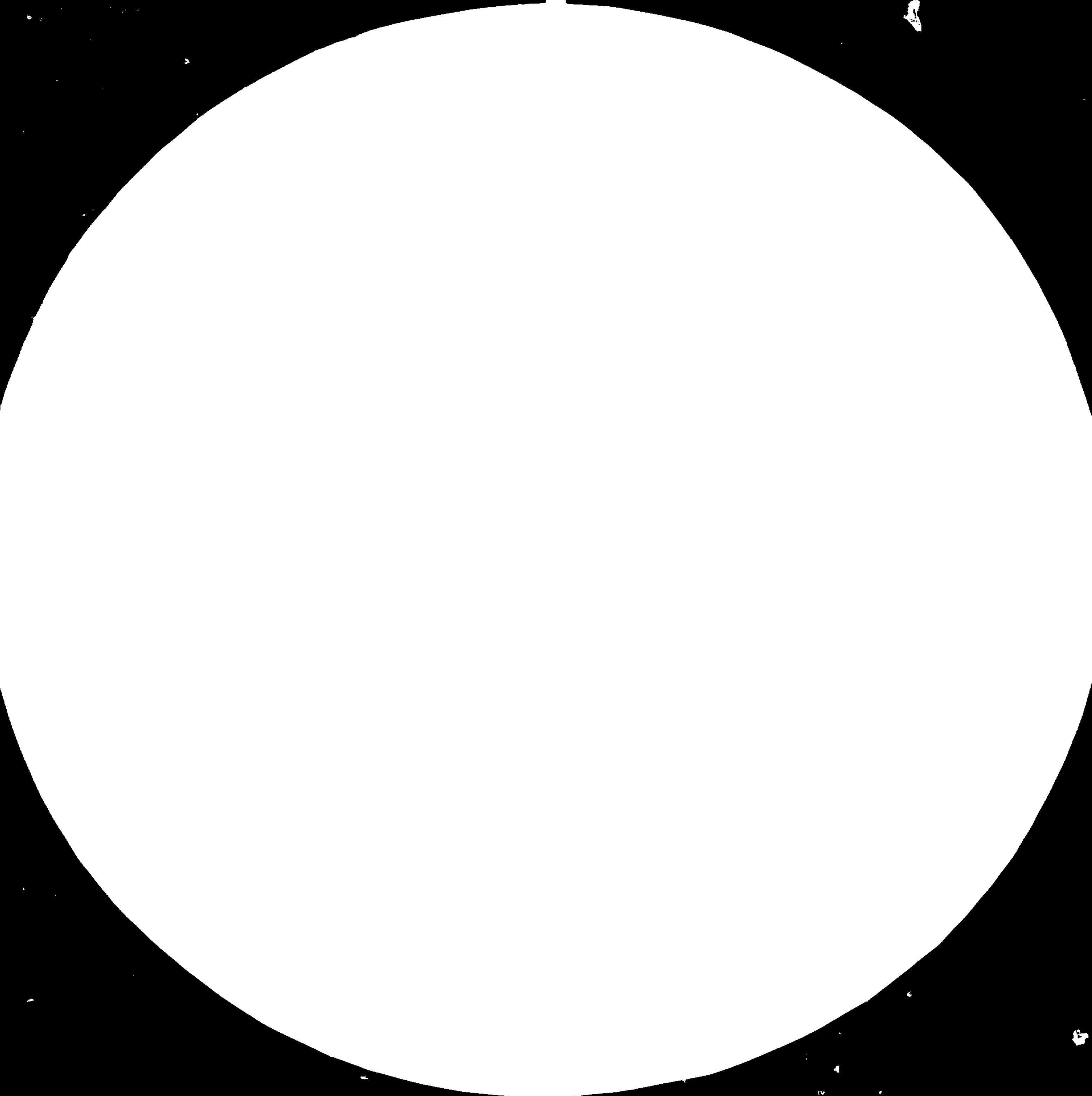

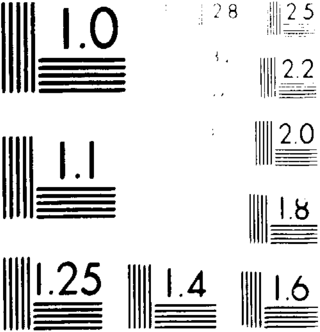
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Energy Conservation in the Aluminium Industry

UNIDO Contract No. 82/76

Report of Visit by E. Bernhauser and P. Reinert

to the

ALUMINIUM SMELTER ZHENGZHOU

November 14 to 26, 1982

February 1983

Member of the Alusuisse Engineering Group

UNIDO Contract No. 82/76

Energy conservation in aluminium industry

List of annexes

Analysis of anode samples

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Improvement of the casting with cast-iron of collector bars in large length cathodic carbon blocks

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Prebaked anodes, analysis methods

Application in pilot plant work in prebaked anode manufacturing

ENERGY CONSERVATION IN ALUMINIUM INDUSTRY

RECOMMENDATIONS FOR IMPROVEMENTS OF THE SPECIFIC ENERGY CONSUMPTION AT THE ALUMINIUM SMELTER ZHENGZHOU

1. Ingress

The smelter Zhengzhou is operated with locally produced anodes and alumina. The reported specific energy consumption of 14.5 kWh/kg Al is reflecting a well controlled operation, however the reported current efficiency of 87 % and the shape of the anode butts prove an extremely small AC distance. The calculated AC distance of 4.4 cm is in the same order of magnitude as the values measured in the pots.

An analysis of two pieces of anodes (see Annex 1) shows that a good anode quality is available, however it has to be stressed that two samples do not conclusively show normal variations of the quality. For a good and stable operation a good average anode quality and a small standard deviation are a necessity.

The results of the analysed alumina sample (see annex 2) are indicating that this type is not suitable for a point feeding system and a dry gas cleaning process. The main deficiencies are the low BET surface of only 20 m^2g^{-1} and the high percentage of fines below 44 μm. According to the Alusuisse experience the alumina fabrication process has to be changed in such a way that the fines are reduced below 10 % and a minimum BET surface of 30 m^2g^{-1} is obtained, which makes the alumina suitable for the point feeding system and dry adsorption process.

2. Possible improvements with low investment costs

2.1 Electrolysis

2.1.1 Reduction of the voltage drops

The present voltage drops are as follows:

0.158 V	busbars
0.366 V	anode
0.456 V	cathode
3.05 V	bath

The connections between anodestub and carbon as well as between cathodeblock and collectorbar can be improved by 0.03 V to 0.05 V each, resulting in an approximately 0.3 kWh/kg Al lower specific energy consumption, provided the heat balance of the pot is adapted accordingly.

To improve the contact stub-anode it is necessary to clean the ironstubs completely from carbon, electrolyte and reaction products (ironoxides and -sulphides) and to use an optimized stubhole design with an increased contact surface. A reduction of the stub hole diameter reduces the shrinkage of the cast iron and improves the contact with the carbon during the first few hours of the anode life in the pots. As a side effect less cast iron (10-20 %) has to be molten.

The replacement of the ramming mix by cast iron can improve the voltage drop in the cathode up to 100 mV. The technique of casting is described in a paper written by D.Dumas and J. Vallon (see Annex 3).

2.1.2 Electrolyte composition

The electrolyte presently in use is composed of

5.1 % AlF_3 (Ratio 1.33)
3.5 % CaF_2

and has a calculated liquidus temperature of 991°C with 1% Al_2O_3 and 973°C with 4% Al_2O_3. The formula used for this calucation (developed by Dewing) has a standard deviation of 3.5°C.

The actual working temperature of 965°C, which is below liquidus indicates that each crustbreaking and anode change produces sediments on the cathodes and increases the contact resistivity between metal and cathode block.

The specific electrical resistivity of the above mentioned type of electrolyte (4% Al_2O_3, 965°C) is calculated at 0.439 Ωcm.

A change to a lithiumtype bath will reduce the resistivity, the working temperature, and the fluoride emissions and improve the current efficiency.

It is recommended to operate a few test cells with the following parameters:

5.8% AlF_2 (bath ratio 1.30)
3.5% CaF_2
6.0% Li_3AlF_6 (2.9% LiF)
955°C bath temperature

This type of bath has a liquidus temperature of 961°C (1 % Al_2O_3) resp. 942°C (4% Al_2O_3). The specific resistivity at 955°C is 0.4306 Ωcm and will allow a slightly increased AC distance (4.5 cm) with the same bath voltage. We expect an increase of the current efficiency to 88%, which means that the energy consumption can be reduced from 14.5 to 14.4 kWh/kgAl. As a side effect a minor reduction of the anode consumption will result as well as a lower flourine ion consumption (approx. 2 kgF/tAl). During the first six to eight months the lithiumcarbonate consumption is above normal because considerable quantities are required for the saturation of the lining of the pots.

The aluminium produced with this lithium electrolite will contain up to 20 ppm Li which has to be removed before producing special products e.g. foil stock.

2.1.3 Anode size

With the present anode size of 1100 x 400 mm an anodic current density of 0.85 A cm^{-2} results with a line current of 75 kA. The dimensions of the potshell and lining allow a minimum anode size of 1250 x 400 mm. The increased anode surface can be utilised either to increase the current intensity or to increase the AC distance in the pots.

As a first step we recommend to increase the line current to 77 kA (anodic current density : 0.77 A cm^{-2}) without changing the set voltage of the pots. This step will increase the AC-Distance of the pots to 5.0 cm and we expect an improved current efficiency of 89 % with the present pot voltage of 4.25 V. The specific energy consumption should be reduced to 14.2 kWh/kg Al. Thus the productivity of the pots should reach 551 kg per pot-day compared with the present 526 kg. As a side effect the specific anode consumption should sink to less than 0.59 kg/kgAl.

2.1.4 Optimizing parameters and procedures

Further improvements, which cannot be quantified without detailed analysis, are possible by optimizing the deviations by anode setting, aluminium fluoride and alumina content of the electrolyte, metal heights and other parameters.

2.2 Anode fabrication

Despite the good anode quality indicated by the two samples analysed by Alusuisse, there are several opportunities to save energy and costs within the fabrication process of prebaked anodes. The main issues are :

- recycling of anode butts
- constant anode quality by means of close quality control
- reduction of fuel oil consumption in the baking furnace
- reduction of the pitch content in the green anodes

An estimate of the savings is only possible after a detailed evaluation of the operating parameters by an expert in anode fabrication.

It is however recommended, that the quality should be monitored on a continuous basis. For this purpose, equipment to measure the reactivity and the permeability of the anodes should be procured. In a further step, we recommended to install a pilot plant for anode production in the research institute. This pilot plant would allow to adapt the recipes and the operation parameters to the different qualities of raw materials and to investigate the influence of deviations in these parameters.

3. Retrofitting of the pots

If a considerable improvement of the energy consumption and current efficiency is envisaged, it is necessary to change the pot design.

The retrofitting concept for the pots itself would be similar to the one used in the Alusuisse smelter at Steg (Switzerland). The pointfeeder is the same proven unit, the metering device has to be adapted to the pot size of Zhengzhou.

For a successful retrofit programme we recommend the following steps:

- adapt the physical properties of the alumina to the requirements of a pointfeeder operation. According to the Alusuisse experience a low calcined coarse alumina is required.

- The magnetic and thermal conditions of the pot should be optimized. It is obvious that the raiser bars only on one side have a negative effect on the liquid metal pad in the pot. This influence can be reduced partially by increased metal height in the pots. Modification of the busbar system will result in a reduction of stirring effects and the doming of the liquid metal surface. This will allow to operate the pots with reduced metal pads at minimum AC distance and maximum current efficiency (92-93%). The exact solution can only be selected after extensive calculations have been made. After a magnetic optimisation of the pot, the thermic balance has to be reevaluated and the optimum insulation and current intensity of the pot has to be determinated. Depending on the degree of optimisation the cost of the retrofit are varying widely, the same applies for the specific energy consumption.

  The reduced stirring effect will also reduce the wear on the side of the cathode lining.

- The operation of a test group of a minimum of 6 modified pots is needed for the evaluation of the hardware, local raw materials and operation parameters.

  We expect that a retrofitted pot with pointfeeders and an optimized busbar system will achieve a current efficiency of more than 90 % and a specific energy consumption of 13.5 to 14.0 kWh/kgAl depending on the degree of optimisation. The anode consumption can be reduced by 10%.

4. Services offered by Alusuisse

4.1 Operation manuals, electrolysis

We recommend that an Alusuisse expert prepares an operation manual for the operation of the sideworked pots. It is foreseen that this work has to be done in Zhengzhou in close cooperation with the local specialists. The operation manual will cover the improvements mentioned under 2.1.1., 2.1.2., 2.1.3. and 2.1.4.

We expect this manual to be elaborated within one month including travelling time to China and back to Switzerland.

The price for this service is Sfr. 70'000.- including travelling expenses.

4.2 Operation manuals, anode fabrication

It is recommended that an Alusuisse expert analyses the operation and prepares an operation manual for the paste plant and baking furnaces. This manual will cover the improvements mentioned under 2.2 and will be elaborated in close cooperation with the local experts in Zhengzhou.

The price for this service is Sfr. 80'000.- including travelling expenses.

For the future improvement of the production parameters we first need significant information about the actual anode properties.

For this purpose we should receive as soon as possible 40-60 anode samples with the following dimensions:

diameter	50 mm
length	min. 160 mm

If above samples are sent in due time it shall be possible to discuss the various parameters during the client's planned visit to the Carbon Research and Development Laboratory in Chippis, Switzerland.

4.3 Measuring equipment

We recommend the following additional equipment to be bought,

- for the smelter:

  - 2-3 measuring tongues for measuring the current distribution in the anodic and cathodic part of the pots.

    Price: Sfr. 8'300.- each ex Chippis, Switzerland (excluding freight).

    Details of this instrument may be seen from the Annex No. 4.

- for the anode plant: (Annex 5 and 6)

  We recommend the installation of a laboratory in order to determine the quality of baked anodes in principle consisting of:

- Core drilling machine CDM	(C-120)
- Resistivity and flexibility apparatus	(C-126)
- Reactivity unit R-6 automat	(C-127)
	(C-128)
- Air permeability apparatus	(C-129)
- Sample preparation: Saw, drying furnace, crusher, balances	

Approx. budget price incl. spare parts of above equipment	sFr. 300'000.-

Option:
X-Ray unit for the determination of the elements (C-124) incl. tablet press

Approx. budget price	sFr. 490'000.-

- <u>for the research institute:</u>

We recommend the installation of a pilot plant for the anode production.

For the determination of the raw material properties we propose that you send 500 kg of coke and 200 kg pitch to:

Swiss Aluminium Ltd.
Research and Development Carbon
Attn. Mr. W.C. Fischer
CH-3965 Chippis / Switzerland

These materials will be used for pilot plant evaluations acc. to AIME-Paper, see annex 7.

Price and conditions for the equipment, the installation of the pilot plant and operation procedures can be indicated after a further discussion with the client.

4.4 Magnetical and thermal optimation of the pot.

ALUSUISSE has developed mathematical models for the simulation and calculation of the magnetic fields in the potroom and for the energy (heat) balance in the pots.

The procedure for the optimation is a combination of computer calculation and detailed design work, which has to be carried out hand in hand. The problem of this method is of course, that only after extensive calculations and design work the result and the amount of work involved can be judged. Already a minor modification of the busbar system could prove to be sufficient to improve the situation considerably, or on the other hand the busbar system may have to be completely modified. The result will be a lower energy consumption or, if this is more desirable, a higher production with similar operational figures.

4.5 Basic Engineering for "Pointfeeder-Pots"

ALUSUISSE is in a position to provide to the client the basic engineering for the pointfeeder pots. It would consist mainly of general arrangement drawings and of detailed drawings of such main items as the measuring device for the alumina. The client would have to adapt the design to the local conditions and to the existing pot design. Such detail design work should be done in close cooperation with ALUSUISSE.

Beside the pointfeeder and the metering device, the package would consist of the hooding of the pots and of the dense phase transport system. Also performance specifications and basic description of the dry adsorption plant could be included.

The package would comprise the mechanical design and the necessary control system.

4.6 Process Control

ALUSUISSE has developed a computer operated process control system, which has been in successful operation at several smelters for several years. Beside the control of the pot resistance, the system allows to predict and, if desirable, to prevent anode effects, to detect noisy pots at an early stage, to monitor the metal tapping and, in combination with the pointfeeder and the dense phase transport system, to control the alumina feeding, etc. Furthermore various kinds of information and operation statistics can be obtained.

The hardware of the control system consists mainly of one micro computer for each two pots. These micro computers are connected to a main frame computer. This arrangement allows to obtain a large part of intelligence at the pot level, a fact that allows the control of the pots automatically even when the main frame computer or the interconnections are out of order.

4.7 Adapting the Alumina Quality

ALUSUISSE has the know-how to modify the existing process and the equipment in the alumina plant to allow the production of alumina which can be used in pointfeeders and in the dense phase transport system.

ALUSUISSE is at present discussing the same procedure for the alumina plant in Guizhou with the Ministry of Metallurgical Industries and the plant in Zhengzhou could be discussed simultaneously.

4.8 Further Procedure for the "Retrofit"

The services mentioned under item 4.4, 4.5 and 4.6 would form a package for the "Retrofit". It is very difficult to judge the results and the benefits that can be obtained by the use of one of the above items alone.

It is therefore proposed to discuss during the forthcoming visit (see item 5) a scope which is acceptable to both parties.

The cost for the relevant services can be agreed upon later.

5. Proposed study tour of Chinese Specialists to Europe

As already agreed in the contract with UNIDO, ALUSUISSE will allow Chinese specialists to visit some of its plants in Europe. The following schedule is proposed :

First day : Visit to the smelter in Fusina near Venice, Italy. This smelter is equipped with 100 kA prebake open pots and is in operation since 1964.

Second day : Visit to the smelter in Porto Marghera (about 10 km from Fusina). This smelter is equipped with 50 kA prebake open pots, comparable to the pots in the Zhengzhou Plant.

Third day : Visit to the smelter in Steg, Valais in Switzerland. This smelter is equipped with the same pots as Fusina, but it has been retrofitted in 1981.

Fourth day : Visit to the smelter in Chippis, Valais in Switzerland. This smelter has similar pots as in Porto Marghera but has been retrofitted with "local fume extraction".

Visit to the pilot plant for anode production in the research laboratory and information about R and D in the ALUSUISSE group.

Travel to Zurich.

Fifth day : Head office Zürich. Final discussion, information about engineering activities of ALUSUISSE.

This programme is a proposal and details can be adapted to the needs of the delegation.

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1) Analysis of anode samples

2) Analysis of alumina

3) Improvement of the casting with cast-iron of collector bars in large length cathodic carbon blocks

4) Clamp on DC-ammeter

5) Development of anode quality criteria by statistical evaluation of operational results in the electrolysis

6) Prebaked anodes, analysis methods

7) Application in pilot plant work in prebaked anode manufacturing

Alesa Alusuisse Engineering, Ltd.

ANNEX 1

Analysis of Anode samples from the Smelter Zhengzhou

Annex 1 to Report on Energy Conservation in the Alumina Industry.

Analysis of Anode samples from the Smelter Zhengzhou

1) Chemical analysis

ash content	0.35 %
iron (Fe)	0.076%
silicon (Si)	0,037%
sulphur (S)	0.85 %
vanadium (V)	0.002%
sodium (Na)	0.05 %
calcium (Ca)	0.011%
lead (Pb)	0.003%
nickel (Ni)	0.021%
manganese (Mn))	traces
potassium (K))	
zink (Zn))	

2) physical analysis

apparent density	1.59 g cm^{-3}
real density (xylene)	2.04 g cm^{-3}
el. resistivity	$< 60\ \Omega\, mm^2\, m^{-1}$
* reactivity RCO_2	6 %
* reactivity test residue	91 %
* reactivity test dust	3 %

* test developed by Alusuisse for measuring Anode quality. Values for residue $\geq$85 % and dust $\leq$ 4 % are indicating a good anode quality.

ANNEX 2

Analysis of Alumina from the Smelter Zhengzhou

Annex 2 to Report on Energy Conservation in the Alumina Industry.

Analysis of alumina from the Smelter Zhengzhou

1) Chemical analysis (dried material)

Na_2O	0.34 %
SiO_2	0.020%
Fe_2O_3	0.019%
V_2O_5	0.003%
TiO_2	0.004%
P_2O_5	$<$0.001%
CaO	0.012%
LOI	0.25 %

2) physical analysis

Grain distribution (microtrac)

$<$ 176 µm	100 %
$<$ 125 µm	97 %
$<$ 88 µm	79 %
$<$ 62 µm	57 %
$<$ 44 µm	36 %
$<$ 31 µm	20 %
$<$ 22 µm	9 %
$<$ 15 µm	4 %
$<$ 11 µm	1 %

BET surface	20 $m^2\ g^{-1}$
α - content	51 %
real density	3.72 $g\ cm^{-3}$
apparent density	990 $g\ dm^{-3}$
angle of repose	33°
static flow angle	$>$70°, alumina does not flow free

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ANNEX 3

Improvement of the Casting with Cast-Iron of Collector Bars in large length Cathodic Carbon Blocks

IMPROVEMENT OF THE CASTING WITH CAST-IRON OF COLLECTOR BARS IN LARGE LENGTH CATHODIC CARBON BLOCKS

D. Dumas and J. Vallon

Abstract

Casting with cast-iron of collector bars in cathodic carbon blocks, used in the industrial cells for aluminium production, is a very severe operation. Thermal shock can produce, specially in long blocks, transversal cracks. We present methods allowing us to cast a collector bar without damage for the blocks.

Dr. D. Dumas is Chief of the Research Laboratory, J. Vallon is Staff Scientist at the Research Laboratory of the Societe des Electrodes et Réfractaires "Savoie", 10, rue de l'Industrie, 69631 Vénissieux (France).

I - INTRODUCTION

The hearth of the industrial pot used for aluminium production, through the electrolysis of a cryolite-alumina bath, is generally built with pre-baked carbon blocks made from anthracite, graphite or other carbon materials. These blocks are grooved, which allows to fix a collector bar linked to the conductors located outside the pot. To make a good electrical contact between bar and block, we use two methods :

- either ramming of a carbon paste,

- or casting, through usual smelting technics, of a liquid metal inside the slot, round the collector bar, after bar and block preheating. We generally use phosphorous cast-iron with a high rate of silicon in order to improve its flowing.

The casting process with cast-iron is adapted to a mass production and, in case of pots using pre-baked anodes with power-carriers sealed with cast-iron, the supplementary investment is low. However, this process presents two disadvantages :

- it needs a careful bar and block pre-heating to avoid a too quick solidification of the cast-iron, which would induce a bad casting (inclusions formation) ;

- it keeps the block through a very strong thermal shock, which, sometimes, involves the appearance of transversal cracks on the external edges of the slot side. These cracks, which do not appear on short blocks, become more and more frequent and important in case of very long blocks ;

- during the cooling of the blocks, cracks - called V cracks - may also happen at the end of the blocks.

For some years, pot sizes were continually developed. Current intensity increased with equal current density, so cathode surface of pots became more than twice larger in the new cells during less time than ten years. In the same time, bottom long blocks mounting took the place of short blocks mounting. Now, about three meters long blocks are not rare in the pots. From these values, transversal cracks appeared to us to be unavoidable, with usual way, whatever may be :

- the cross-section of the block,
- the dimensions of the slot,
- the cross-section of the collector bar,
- the kind of the block,
- the composition of the cast-iron.

Then, transversal cracks, which conduce to a weakening of mechanical characteristics of the block, in relation with tension, are probably harmful to the life of the pot.

Then, we would like to show how it is possible to modify the usual casting process to obtain a decreasing, or even, a total elimination of transversal cracking risks in the blocks.

II - USUAL CASTING PROCESS WITH CAST-IRON

After cleaning by shot-blasting, the collector bar is set in the slot. We place it on iron-shim or on asbestos rope so as to obtain a space between bar and slot for the flowing of the cast-iron. This space is carefully taped at the block ends, with a cement or asbestos rope, or even both, to avoid a leak.

Then, we preheat both, bar and block, with a duration of preheating from 2 to 5 hours, according to the plant equipment. As we want to preheat specially the bar and the part of the block in contact with cast-iron, the heating is generally done by using gas or oil burners, which are directed straight on the bar. Sometimes we use a furnace with electrical heating or radiant gas burners, inside of which bar and block are placed. The latter process offers the advantage to eliminate humidity from block which is an other source of damage during casting.

The temperatures we reach on preheating and which lead to a correct casting are the following :

- temperature : 400° to 700°C in the middle of the bar,
- " : 250° to 450°C inside the block, near the slot,
- " : 1250° to 1500°C for the cast-iron at casting-time.

The casting operation is fast (some 10-20 seconds per block). On the other hand, between the moment when the preheating is stopped and the moment of casting, there is sometimes a 10 minutes interval which brings a decrease of the preheating temperature. The cast-iron is poured in the slot with a "casting pot" that we go to fill in, after preheating, to a smelting furnace (induction of fuel furnace or, sometimes, cupola). As the casting ends, the top of the block is covered with an insulator to avoid a too fast cooling of the upper part of the bar.

III - STUDY OF THE THERMAL SHOCK IN CARBON CATHODE BLOCKS

1. Introduction : Transversal cracks (Figure 1)

These cracks appear a few minutes after casting (from 2 to 3 minutes) ; they seem to start from the block edges and spread on a plan normal to the longitudinal axis of the block. In most cases cracks are relatively short, i.e. they spread from side to side of the edge and are no more than 5 or 7 cm in length. In most serious cases, they pass through a part of the block and affect a surface greater than half section. Only one crack or more (two or three) may appear on each face. The cracks progressively close again and disappear while the block becomes isotherm. Generally, it is impossible to see them a few hours later. These are thermal shock cracks which are the consequence of the strength induced by the heterogeneous expansion resulting from the high gradient of temperature in the block wings. So, when cast-iron is poured in the slot, the faces of the slot are suddenly heated. The superficial layer expands more quickly than the internal of the wings and is submitted to a compressive strength while the internal is in tension. These stresses are set in a parallel direction to the bar and proportional to :

- the expansion coefficient,
- the thermal gradient which is correlated to the thermal properties of the blocks. The part of the block under gradient cannot bent to release the stresses which tend to cause cracks at the weakest point.

2. Thermal shock studies

We studied in carbon blocks the thermal shock wave by means of thermocouples placed in some points, specially in the wings. We can note, Figure 2, the place of the thermocouples in the trial blocks. Figure 3, we showed a typical registration of the temperatures variation versus the time for the different thermocouples.

We can note the following remarks :

- The thermal shock reaches his maximal value within two or three minutes after casting.
- When the temperature is maximal near the face of the slot, its value in the middle of the wing has not yet changed.
- The temperature of the base of the block does not change.
- The temperature gradient decreases very quickly.

So, we note that the thermal gradient can be extremely high.

If we want to decrease the risks of transversal cracks, first we can attempt to keep the thermal shock lower by working :

- either on the temperature,
- or on the quantity of cast-iron.

Casting with blocks, the slot of which was different, showed the influence of the amount of cast-iron (Table I). The results are relative to blocks the length of which is less than 2.5 meters with a cast-iron temperature between 1250 and 1300°C.

Table I

Trial reference	Slot section (dm2)	Collector Bar Section (dm2)	Cast-iron section (dm2)	Number of casting	Results*
1	2.48	1.68	0.80	A lot	A few
2	2.63	1.68	0.95	8	0
3	2.78	1.68	1.10	20	25
4	2.48	1.04	1.44	A lot	50
5	2.48	0.81	1.67	1	100
6	1.62	No Bar	1.62	3	100

* The results are plotted in percentage of blocks with transversal cracks.

The studies of the thermal shock, and the experiments we made, showed that we have a limitation of both parameters, temperature and amount of cast-iron. Below a certain level, casting becomes difficult and risky.

Anyway, beyond a certain length of the blocks, it becomes very difficult, or even impossible, to avoid transversal cracking. The casting process we present allowed to avoid these disadvantages :

- either by improving the existing preheating method in order to reduce the thermal shock,

- or by a process tending to prevent the formation of stresses in the block.

IV - IMPROVEMENT OF CASTING PROCESS

It was advisable to work out casting process avoiding cracking risks :

- either by decreasing thermal gradients in the block wings,

- or by preventing the appearance of stresses.

In the former case, we will keep the thermal shock at a low level by an improved preheating process, and in the latter case we will get the block wings in pre-strengthening conditions.

1. Improvement of casting process by using a lateral preheating (B.F. 72/09 362, March 17th, 1972).

The ordinary preheating processes do not generally go towards a decreasing of the thermal shock. Effectively, the preheating of the collector bar must be important to get a suitable temperature inside the slot to avoid a too quick freezing of the cast-iron. But, if such preheating is too high, the bar will not absorb most of the heat brought by the cast-iron ; what will increase the thermal shock inside the block. Furthermore, if the preheating time is too long, a too high temperature conduces to an important oxydation of the carbon block near the slot.

The process consisting in a lateral preheating has less disadvantages. We preheat both, block and collector bar, by applying the heating simultaneously :

- on the collector bar,
- on the lateral longitudinal surfaces of the block,

setting in the slot, on both sides of the bar, a thermal insulator (such as asbestos sheets), to avoid thermal diffusion from the bar to the wings, which we will remove at the moment of casting.

This double heating offers the following advantage :

- The lateral preheating of the surfaces produces in the wings of the block a reverse temperature gradient opposite to that one which is developed either by a usual preheating, or by the casting process. As a matter of fact, the thermal shock is lowered and the percentage of transversal cracks is reduced.

We made tests with three meters long blocks. The cast-iron section was close to one dm2 and the cast-iron temperature was between 1350 and 1450°C. The temperatures measured in the median transversal section of the block, just before we stopped the burners, were the following :

- Collector bar temperature (°C) : 550 - 650
- External faces of the block (°C) : 400 - 450

We produced in the wings of the blocks a reverse gradient close to 70 - 100°C.

As a matter of fact, this process depends on the speed of the casting operation. If the time between the moment we stop the lateral burners and the moment we carry out the casting is relatively long, the gradient decreases and even reduces to zero.

This is pointed out in table II.

Table II

	Collector Bar Temperature (°C)	External faces Temperature (°C)	Waiting time* (minutes)	Thermal Gradient in wings (°C)	Results**
Usual casting process (burners on collector bar)	500-650	150-240	1-3	100-150 unfavourable direction	85
Double preheating casting process	650-700	410-480	1	70-100 favourable direction	0
	550	320-400	6-8	0	75

* Time between the moment we stop the burners and the moment we pour the cast-iron.

** The results are plotted in percentage of blocks with transversal cracks.

2. Improvement of casting process by pre-strengthening of the block wings

(B.F. 72/09 363, March 17th, 1972)

The expansion in a longitudinal direction of the different parts of the block wings tends to follow the temperatures outline and it develops tensile strength in the cold part of the wing. We can decrease the inner stresses through an outer reaction which will consist in compressing the block wings :

- either on the hottest part of the wing to resist the expansions,
- or on the outer part of the wing to resist the inner stresses.

The latter solution needs a weaker outer stress. It is the one we choosed.

Tests were carried out with 3 meters long blocks. The pre-strengthening was applied to the block-wings by the mean of very suitable frame (Figure 4). Test conditions were as follows :

- Cross-section of cast-iron (dm2) : 0,90
- Cast-iron temperature (°C) : 1380-1450
- Collector bar temperature (°C) : 590-650
- Block temperature (°C) : top wings : 400-450
  bottom : 100-150

These temperatures were measured in the medial transversal section of the block. On top of blocks the temperature is measured on the wings as nearer the slot as possible. Down, the temperature is measured below the block.

During the tests, we tried to know the minimal pre-strengthening which can be applied for a minimal time and for a given pre-heating time. The pre-strengthening was applied on a surface of 100 cm2, covering 2/5 of the wing surface.

a) Pre-heating time and pre-strengthening time

We have applied a pre-strengthening of 50 kgf/cm2. On table III, we point out the results in percentage of blocks casted without transversal cracks.

Table III

Pre-heating time (minutes) / Pre-strengthening time (minutes)	120	60	45	30
20	100	-	-	-
10	100	89	0	0
7	-	100	-	-
5	-	50*	-	-

* Pre-strength of 30 kgf/cm2

If we consider that the thermal shock is maximal within the two or three minutes following the casting, we can easily understand that we cannot expect to shorten the pre-strengthening application time which is about 10 minutes. After 10 minutes, the thermal gradient in the block has gone down about 1/3 referring to its maximal value (Figure 3).

b) Value of applied pre-strengthening

The results are collected in Table IV. The pre-strengthening was applied during 10 minutes.

Table IV

Pre-strengthening (kgf/cm2)	Results (% blocks without cracks)	
	Preheating time 1 hour	Preheating time 2 hours
50	89	100
40	66	-
30	50	-
0	0	14

The distribution of the pre-strengthening is certainly not uniform along the block, but it seems that 50 kgf/cm2 is close to the value necessary to avoid transversal cracks. This value is higher than the tensile strength of carbon blocks which is in the range of 25 - 35 kgf/cm2.

V - CONCLUSIONS

From our results, we can see that both methods, lateral preheating and pre-strengthening, are efficient to eliminate almost completely the risks of transversal crackings in the blocks wings. In fact, it seems that the second one is not so difficult to employ and can be used without transformation of the casting work-room. A pre-strengthening of 60 kgf/cm2 rate, applied on about 2/5 of the block wings surface and maintained for more than 10 minutes, can warrant a casting procedure without risks. Forces at stake keep weak, thus the supplementary investment will be reasonable as regard the advantages. The pre-strengthening time lasts shortly enough not to slow the casting rate of the work-room. Moreover, we noted that, taking less care concerning block and bar temperatures, we can reduce the preheating time considerably.

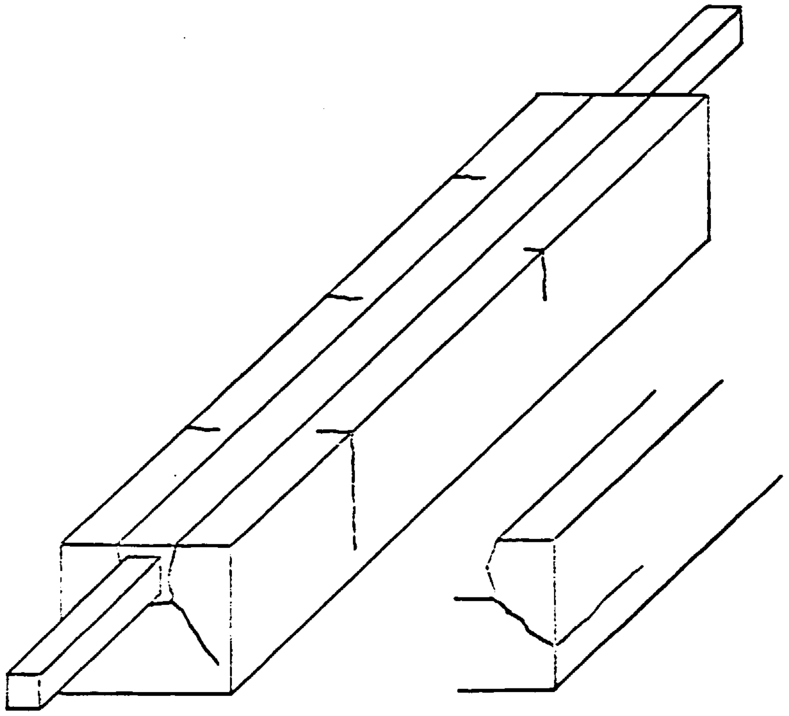


Figure 1

Types of cracks produced in the blocks by casting with cast-iron

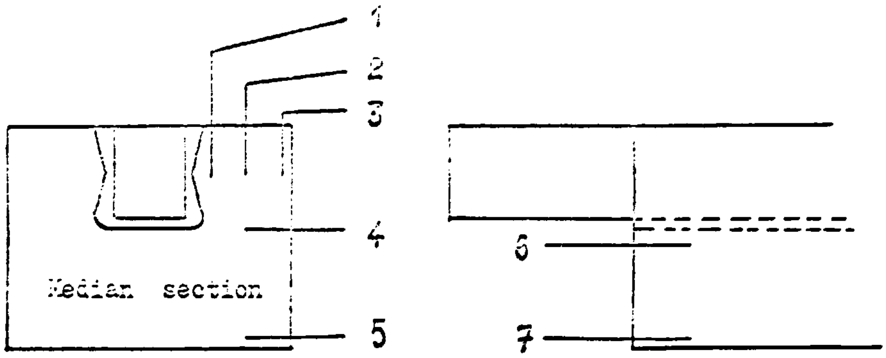
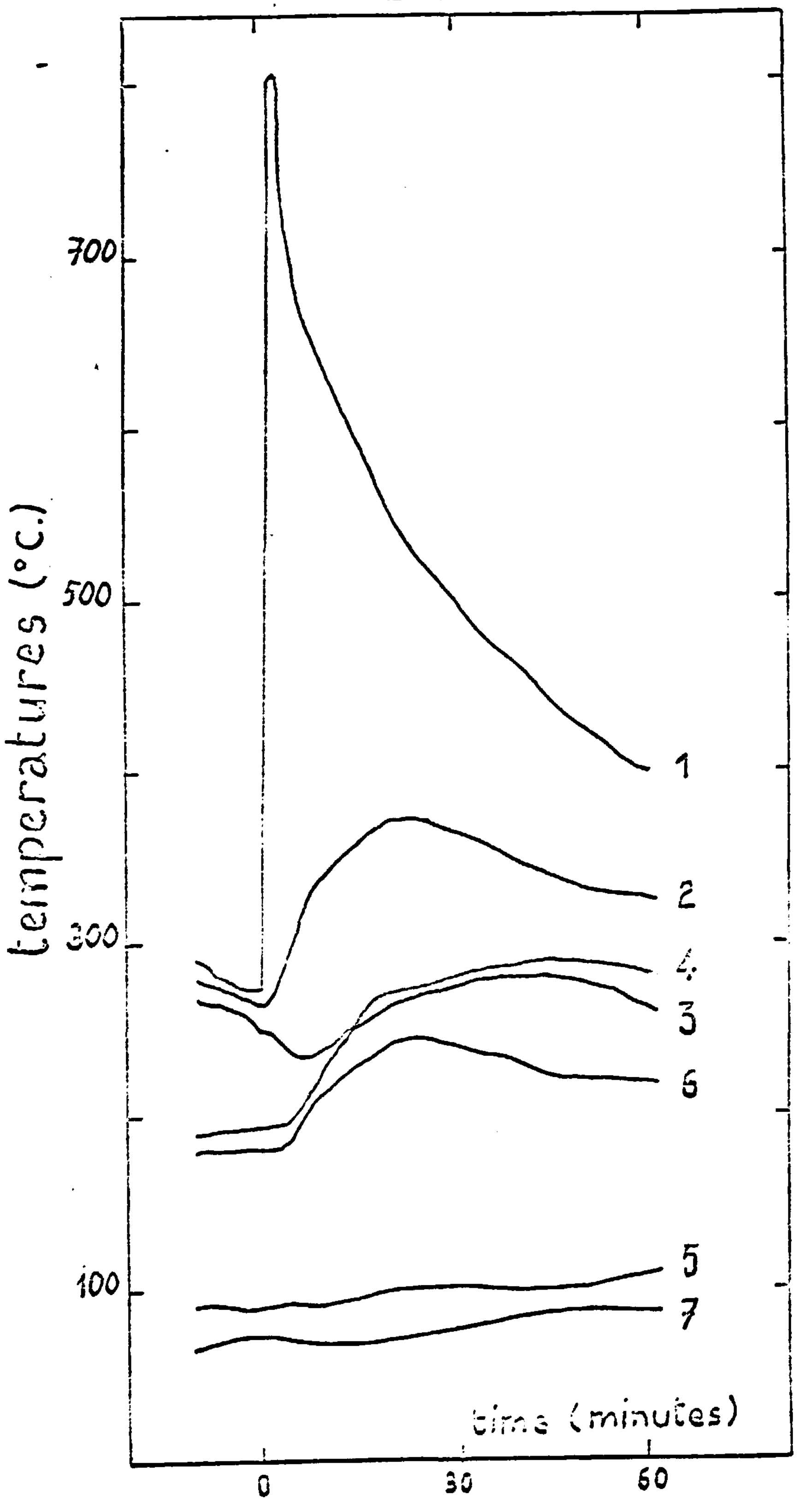


Figure 2

Place of the thermocouples in the blocks

Figure 3



ANNEX 4

Measuring Toungue

Measuring Toungue

1. Purpose

The clamp-on DC ammeter provides an easy means of measuring the high DC currents occuring in potrooms. By clamping a measuring head around a current carrying conductor, the current can be read in kA directly of an instrument. Therefore the current distribution in anode rods and cathode bars can easily be established.

The clampon device used for anodes is equipped with a handle, allowing operation of the measuring head from the potrim. The cathode bar currents are measured with a clamp-on device without handle. Its diameter however is bigger.

2. Theory of operation

As Maxwell has shown, the linear Integral of the magnetic induction along any closed loop is proportional to the current responsable for this induction.

$$\oint B \cdot ds = \mu \cdot \Theta \Longrightarrow \text{prop. } I$$

B: induction
ds: distance unit of the closed loop
μ: magnetic permeability
Θ: total flow through current
I: current

While putting the clamp-on device around the current carrying bus bar, a voltage is beeing induced. An integrator, located in the instrument, forms the voltage-time integral which is proportional to the current in the bus bar.

$$\int U \cdot dt \Longrightarrow \text{prop.} \quad \oint B \cdot ds \Longrightarrow \text{prop. } I$$

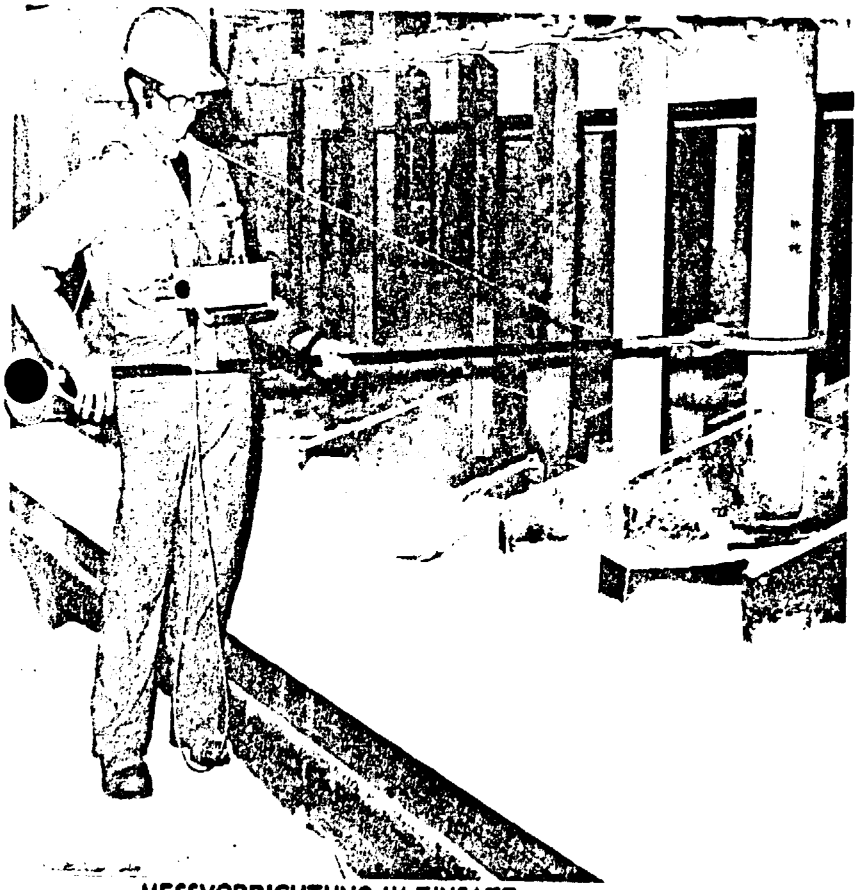
U: measured voltage
dt: time unit

The indicating instrument connected to the output of the integrator therefore can be calibrated directly in kA.

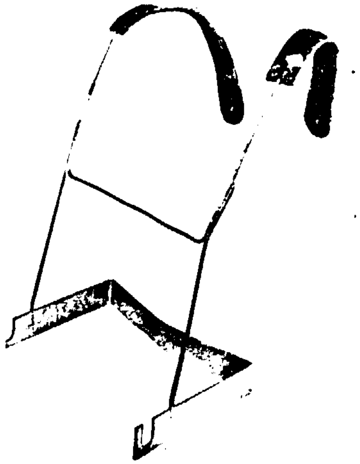
MESSWESEN UND AUTOMATION CHIPPIS

DEZEMBER 1970

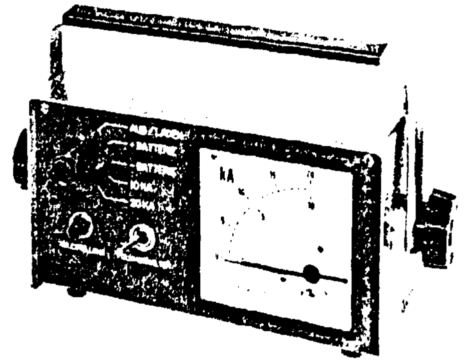
MESSZANGE MODELL 70



MESSVORRICHTUNG IM EINSATZ

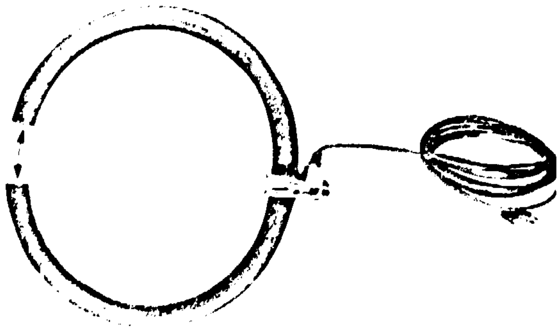


TRAGVORRICHTUNG



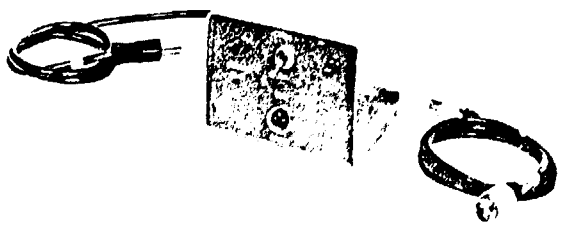
ANZEIGEGERÄT

MESSZANGE FÜR ANODENMESSUNG ø 260mm



MESSZANGE FÜR KATHODENMESSUNG ø 400mm

LADEGERÄT



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ANNEX 5

Developement of Anode Quality Criteria by Statistical Evaluation of Operational Results in the Electrolysis

DEVELOPMENT OF ANODE QUALITY CRITERIA BY STATISTICAL EVALUATION OF OPERATIONAL RESULTS IN THE ELECTROLYSIS

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Switzerland

Anode quality data, measured between 1970 and 1980, were correlated with the operational results of reduction plants.

The relation between reactivity and air permeability of anodes and anode performance in reduction cells was investigated.

Introduction

A comparison of the aluminium production cost of the years 1971 to 1980 shows a tremendous increase of the anode cost portion. In many cases the price of the anodes calculated per ton of metal have surpassed the cost of the electrical energy.

This means that the anodes may play the second most important role after alumina in the production of aluminium. The general trend of the production cost is shown in figure 1.

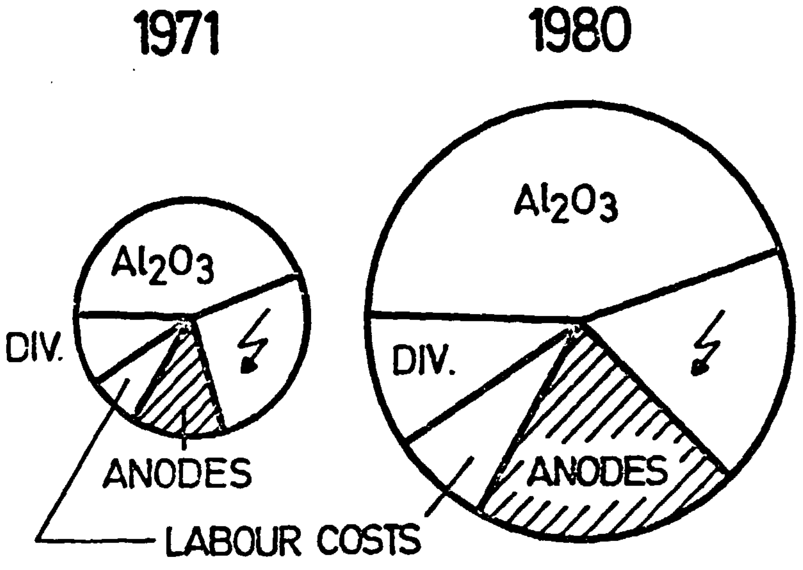

Figure 1 : Development of Al-production costs.

The increase of the anode prices is mainly caused by the skyrocketing costs of anode raw materials. At least of the same importance is the fact, that since several years strong fluctuations in the quality of these raw materials must be taken into account. When advances in process technology used in making the anodes are not made in time to adapt to the changed raw material properties, anode consumption will increase, which will lead to an even higher anode cost portion and in the worst case to severe disruption of potroom operations.

To encounter these problems, Alusuisse has developed methods in pilot plants (1) to optimize the anode quality. With these methods it is possible to determine in a short time the best attainable anode properties with a given raw material. However, not the anode properties are decisive, but the net carbon consumption obtained with such anodes. The answer to the question, which net carbon consumption can be expected with the use of given raw materials, is of upmost importance, especially when a decision has to be made how much money can be spent on the purchase of better raw materials.

It is shown in the next chapters how we succeeded during the recent years to predict the expected net carbon consumption of anodes produced on a large commercial scale.

Determination of anode properties and anode performance

Alusuisse operates an anode production centre at Rotterdam. More than two million tons of anodes were produced for various reduction plants in Europe and overseas during the period of 1970 to 1980. Forwarding these large quantities of anodes to smelters at distant locations requires a thorough quality control system. Every year over 10.000 samples are taken and tested according to the diagram shown in figure 2.

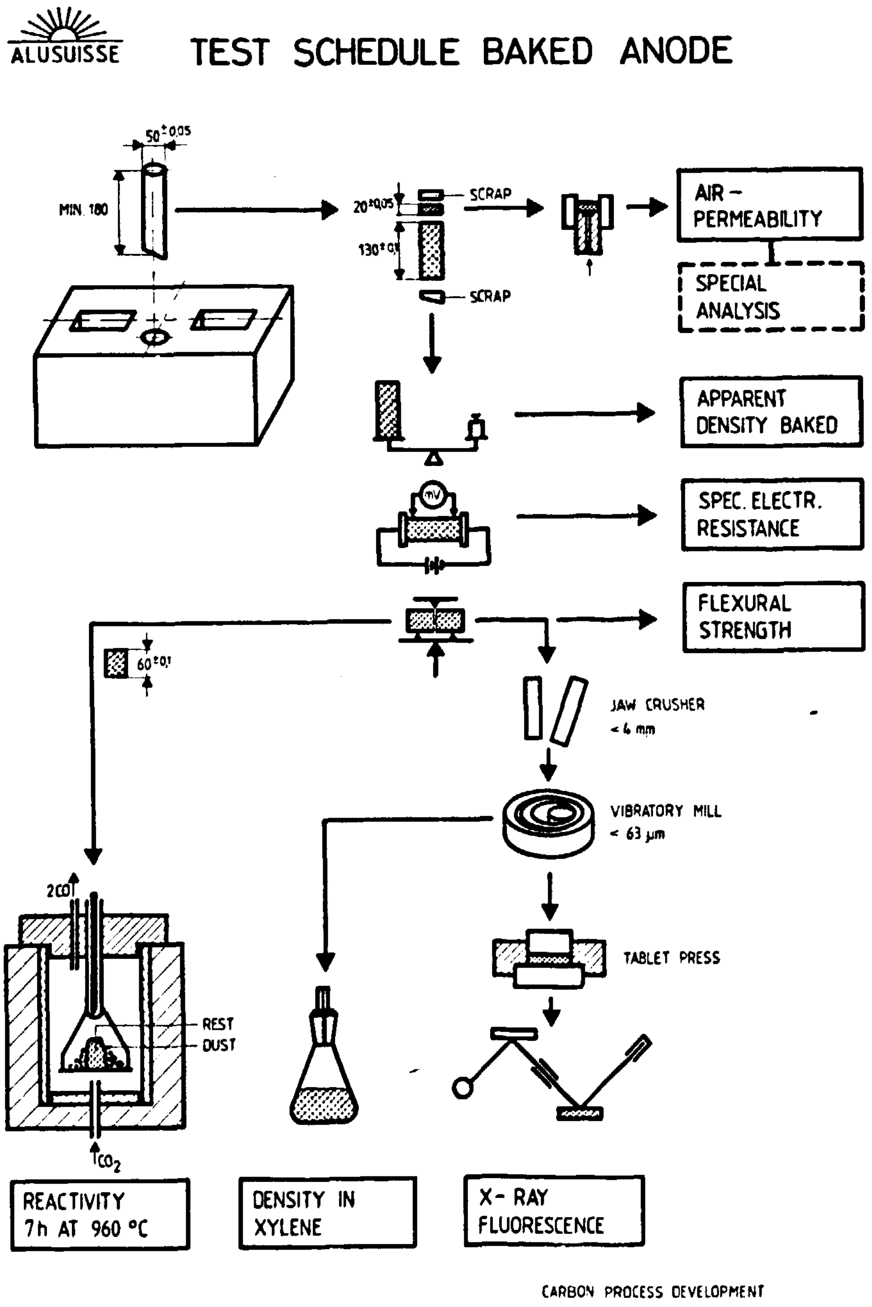

Figure 2.

From every fiftieth anode a cylinder with a diameter of 50 mm and a length of 180 mm is drilled. The following properties are established on each sample, according to the Alusuisse test methods:

- The apparent density is determined by weighing a dry cylinder with prescribed dimensions.
- The specific electrical resistance is determined by measuring the voltage drop.
- The flexural strength is determined by applying a load in the middle between two supports on which the cylinder is positioned.
- The amount of impurities is determined by the use of a X-ray fluorescence apparatus. For reliable results the apparatus requires proper standards for all elements concerned.
- The real density is measured with a pycnometer in xylene according to ISO-Standard 901 (2) on a sample ground to a size of < 63 μm.
- The reactivity is tested by heating a part of the cylinder for 7 hours at 960°C in a CO_2-atmosphere.
- The permeability is determined with an apparatus developed especially for anode carbon. Apparatus and technology are based on the standard method for the determination of permeability of refractory materials according to ASTM-Standard C 577-68 (3). The time is measured which is needed to press a certain amount of air under prescribed conditions through a sample. The result is recorded in Nanoperm (nPm).

The anode performance in the reduction cell is characterized by the excess carbon consumption rate. Normally, anode consumption figures are given as net anode consumption rates. The net consumption consists of the electrolytic consumption and the excess consumption.

The monthly mean values of the anode quality properties were correlated to the corresponding operation results of the potrooms. The next chapter describes the obtained correlations.

Correlations between anode properties and anode performance

The following table 1 shows the range and the typical values on the anode properties of all production lots manufactured during the period of 1970 - 1980. The size of a production lot is about 1.000 tons and the number of production lots taken into account is about 2.000.

	UNIT	PRESSED ANODES		VIBRATED ANODES	
		TYPICAL VALUE	RANGE	TYPICAL VALUE	RANGE
SPEC. ELECTR. RESISTANCE	$\mu\Omega m$	63	51.7 – 74.3	58	50.9 – 64.9
FLEXURAL STRENGTH	$10^5 N/m^2$	80	53.3 – 113.1	115	93.6 – 137.8
APPARENT DENSITY	kg/dm^3	1.530	1.488 – 1.570	1.525	1.481 – 1.567
REAL DENSITY (XYLENE)	kg/dm^3	2.07	2.039 – 2.093	2.07	2.040 – 2.094
REACTIVITY REST	%	80	61.2 – 88.4	80	60.9 – 89.7
DUST	%	7	2.8 – 16.0	7	2.9 – 16.7
AIR PERMEABILITY	nPm	1.2	0.7 – 5.5	1.3	0.8 – 6.2
ELEMENTS			TYP VALUE	RANGE	
Si	%		0.020	0.001 – 0.041	
Fe	%		0.050	0.020 – 0.082	
V	%		0.010	0.004 – 0.020	
S	%		2.00	0.83 – 2.53	
Ti	%		0.001	0.001 – 0.003	
Na	%		0.060	0.007 – 0.113	

Table 1.

The chemical properties are practically identical for pressed and vibrated anodes. The physical properties show, however, significant differences in specific electrical resistance and flexural strength. These differences can be completely explained by the forming process. Remarkable is the practically identical value of the apparent density for pressed and vibrated anodes.

The anodes were used uncoated in side breaked, unhooded reduction cells.

Correlations between anode properties and anode consumption are often described in the literature (4 - 14). Of special interest are the publications of Hollingshead, Hildebrandt, Barrillon, Jones, Ayushin, Hirt and Wilkening. These authors described e.g. the relationship between anode consumption and reactivity performance, apparent density, porosity, surface area, air permeability, specific electrical resistance, etc. of the anodes.

Most of the quantitative results were obtained by laboratory investigations and were confirmed by operating measurements with relatively small numbers of anodes. As far as we know, no results have been published on correlations between anode quality and anode performance, based on a continuous monitoring of anode properties and anode consumption rates in different smelters for a whole decade.

For the analysis of the big amount of figures a hypothesis based on literature study and own research was formulated according formula (1):

Excess carbon consumption = f (Purity, Structure, Porosity) (1)

The excess carbon consumption in the reduction cells is according to this hypothesis a function of the chemical purity, the crystalline structure and the porosity of the anode material.

The chemical purity is analysed as described above. The crystalline structure of the coke is characterized by the height Lc of the crystallites, which can be measured by X-ray diffraction. It is also known, that there is a strong correlation between the height of the crystallites and the true density measured in xylene. We consider the last method as more practicable for large test series. Anode purity and structure are thus very well defined. More complex is the situation with porosity. The total pore structure is generally classified in three ranges : macropores, larger than 50 µm, micropores in the range from 1 to 50 µm and submicropores smaller than 1 µm.

Numerical elaboration of all variables of formula (1), however, was not practical. Only "structure" can be defined by one figure; for "porosity" and even more for "purity" much more figures have to be taken into account. Fortunately advantage could be taken of research that was done for a better understanding of the long-known reactivity test. The results of this research will be presented later in a separate lecture. The conclusions of this research are, that the reactivity is influenced by the three variables purity, structure and microporosity. Furthermore it could be proven that the influence of the submicropores on the excess carbon consumption is much less than assumed in the past. On the other hand the macropores as defined by the permeability have an important influence on excess carbon consumption. Accordingly the hypothesis (1) can be simplified into formula (2):

$$\text{Excess carbon consumption} = f\ (\text{Reactivity, Permeability}) \qquad (2)$$

Although not directly identifiable, this finding corresponds with the results of the authors mentioned previously. They found e.g. correlations between baking temperature, sodium content or apparent density and the excess carbon consumption. These results have been confirmed by our investigations.

For example relations between reactivity, true density and the sodium content could be proven.

A higher true density and a lower sodium content lead to an improved reactivity. A higher density in xylene, which accordingly has a positive influence on carbon consumption, can be obtained by higher baking temperatures ($+ 100^{\circ}C \triangleq 0{,}002\ kg/dm^3$). The sodium content, however, can hardly be reduced by the baking operation.

Another significant proven relation exists between permeability and apparent density (figure 3). The correlation shown is based on physical data measured on anodes of different producers.

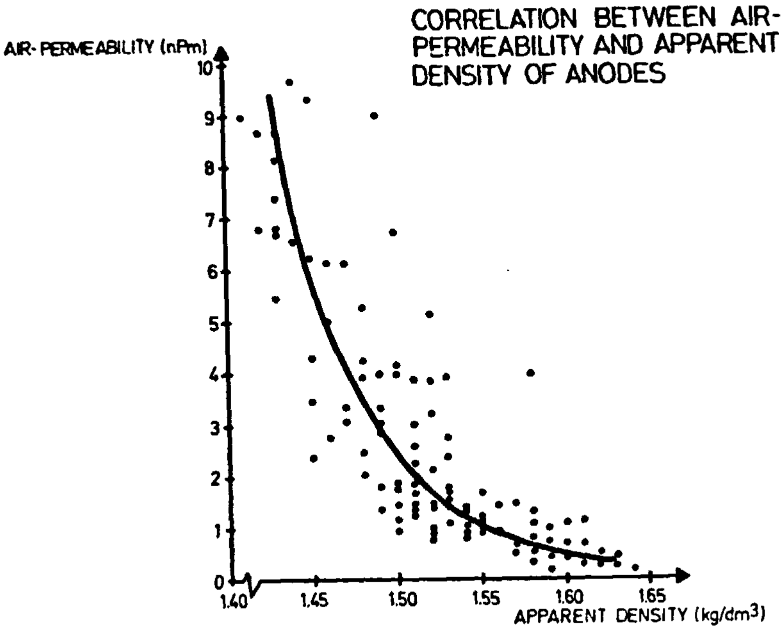

Figure 3.

Figure 3 illustrates that a higher apparent density generally leads to a lower permeability. Strong deviations are, however, also apparent on both sides. Some lots of anodes can have the same density but quite different permeability. A high permeability may be caused by errors in the recipe, a low permeability can be caused by modifications in process technology, especially e.g. concerning the forming process. From this point of view the permeability is of more value than the apparent density. The permeability again has no significant influence on the reactivity test, as this test is performed under isobaric and isothermic conditions.

During the investigation all correlations between the different related variables were established. The simplified hypothesis relating excess carbon consumption to reactivity and permeability could be proven.

Reactivity and permeability should be taken as independent anode properties, which together determine to a great extend the excess consumption of the anodes in the reduction cell.

Prediction of anode consumption

By using multiple regression analysis for the above-mentioned anode populations a quantitative relationship for normal and undisturbed reduction cell operation could be established. According to the final result of the investigation, the optimum attainable net consumption (rather than the excess carbon consumption) can be calculated with equation (3).

$$\boxed{NC = 347 + \frac{334}{\eta} + 9.3\ AP - 3.7\ RR} \qquad (3)$$

NC = Net Consumption in gr_C/kg_{Al}
η = Current efficiency
AP = Air Permeability in nPm
RR = Reactivity "Residue" in %

The permeability of the investigated anodes was in the range of 0.7 - 6.2 nPm. The reactivity "residue" was in the range of 60.9 - 89.7 %. The influence of both factors on the net carbon consumption is about the same. The net carbon consumption is only predicted correctly, if the standard deviations of the anode properties, which influence the oxidation, are under control. It is also assumed that the mean values and the standard deviations of the other anode properties, like flexural strength and electrical resistance, are within the normal range.

Only a preliminary investigation was made to determine the influence of the thermal conductivity. However, the investigated anode populations had a practically constant thermal conductivity.

The factors of the equation have eventually to be varied slightly for different reduction cells and/or for changed operating parameters of the cells. Taking these facts into account, it is possible to predict the attainable net anode consumption for all anodes produced by todays technology.

This result remains correct, if the permeability and the reactivity are influenced by changes in raw material properties or other measures in the process technology. It is also very important, that the data for the equation can be determined with simple methods. The needed equipment is shown in figures 4 and 5.

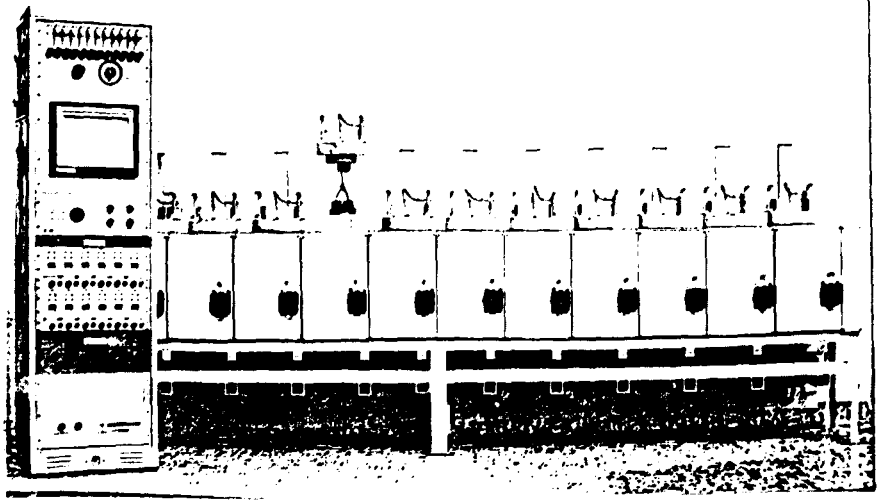

Figure 4 : Apparatus for the determination of the reactivity behaviour of carbon materials. Capacity 48 samples per day.

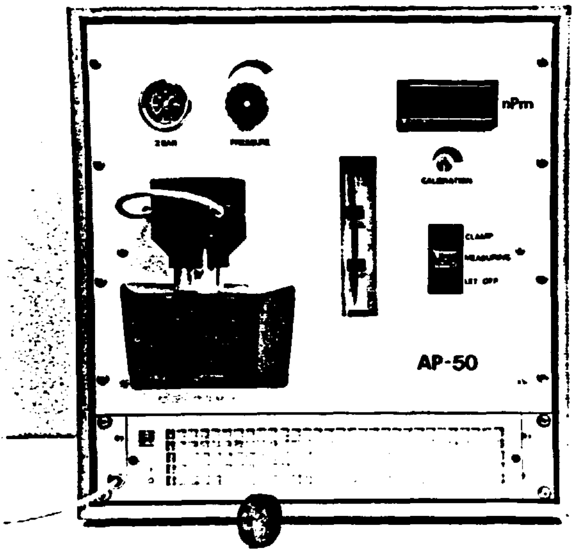

Figure 5 : Apparatus for the determination of the air permeability in the range of 0.1 nPm to 30 nPm.

The practical use of the illustrated relationships can be shown by the following examples.

In one case a petroleum coke quality decrease would have resulted in a reduction of the residue of the reactivity test of approximately 8 % if the production parameters would not have been changed. With the same value of the permeability this would have resulted in an increase of the net carbon consumption of approximately 30 gr_C/kg_{Al}. By appropriate measures in the production process this decrease in anode quality could be avoided.

In another case tests showed that after conversions made for the production of anodes for high purity metal the permeability had increased from 1 nPm to about 5 nPm, with for the rest excellent reactivity values. These anodes would have certainly resulted in disturbance of the reduction cells. Process optimization by use of the pilot plant succeeded in anodes with good reactivity and permeability.

With the above-mentioned formula (3) it is now possible to judge in a quantitative way the anode quality in respect to the performance in the reduction cells. The knowledge of the relationships, the availability of the test methods, and the availability of a pilot plant for process optimization allow the production of an excellent and constant anode quality also under difficult conditions.

Conclusions

- The strong increase of the prices of the anode raw materials has increased the commercial impact of the anodes for the aluminium production.
- The long term availability of good and economical raw materials with a constant quality cannot be guaranteed anymore.
- Process optimization with the use of a pilot plant allows a swift prediction of the expected anode qualities.
- The quantitative relationship between net carbon consumption, and anode reactivity and anode permeability could be established.
- Reactivity and permeability are independent variables: they both determine the net carbon consumption in the reduction cells.
- The established relationship is the basis for the purchase of raw materials, process optimization, and further improvements of anode quality.

Acknowledgements

The authors wish to thank all co-workers who have furnished the necessary data during the past decade.

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ANNEX 6

Prebaked Anodes Analysis Methods

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Prebaked Anodes

Analysis Methods

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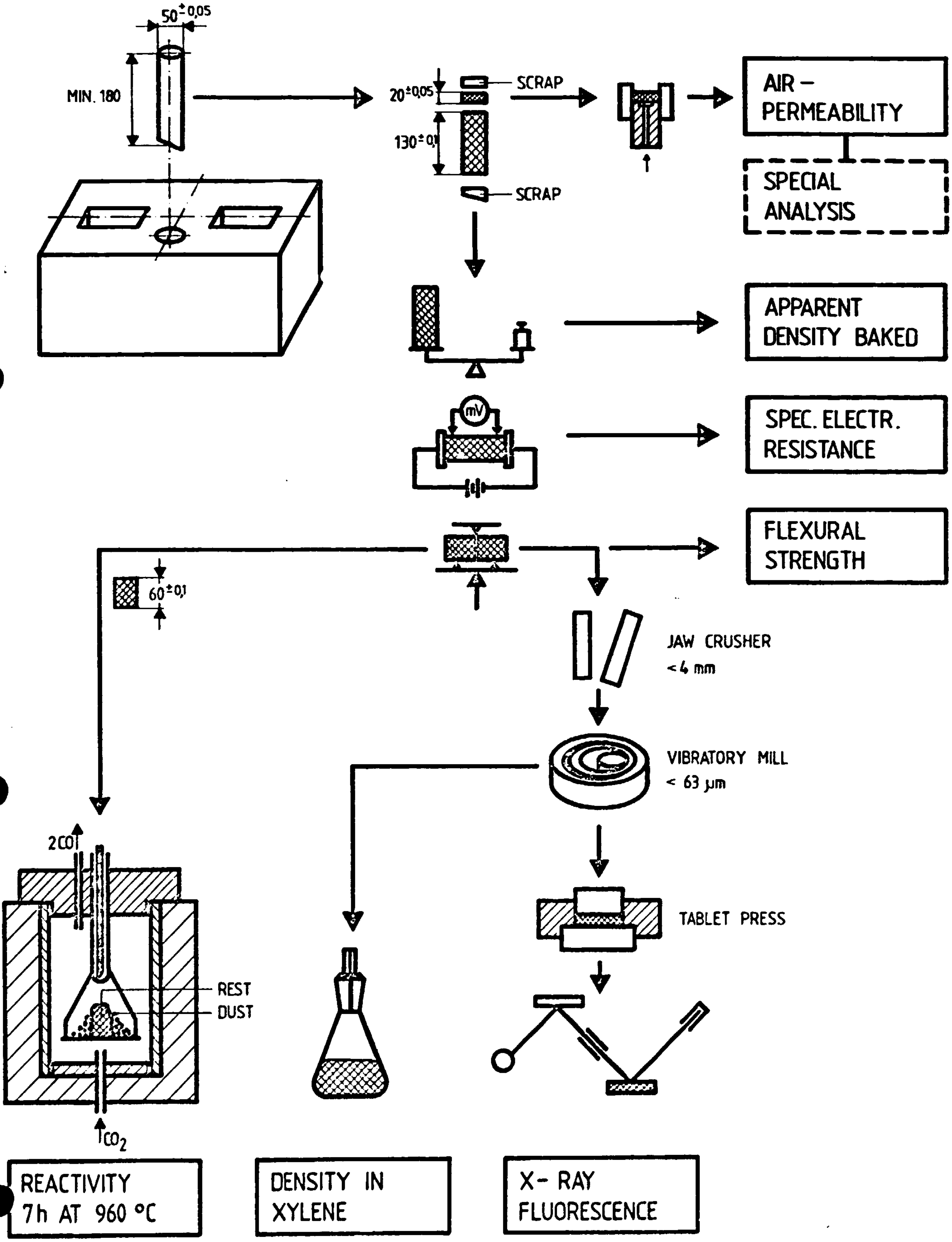
TEST SCHEDULE BAKED ANODE



CARBON PROCESS DEVELOPMENT

ANODENQUALITAT
PROPERTIES OF ANODES

HERSTELLER / MANUFACTURER:
ABNEHMER / CONSUMER:
FORMAT / SIZE: GEPRESST / GERÜTTELT
PRESSED / VIBRATED

70
60
$\overline{X}$
50
SPEZ. EL. WIDERSTAND / SPEC. ELECTR. RESISTANCE μΩm
20
10
2σ
0

150
100
$\overline{X}$
50
BIEGEBRUCHFESTIGKEIT / FLEXIBILITY $10^5 N/m^2$
100
50
2σ
0

1,60
1,55
1,50
$\overline{X}$
1,45
SCHEINBARE DICHTE / APPARENT DENSITY kg/dm^3
0,10
2σ
0,00

95
90
85
80
$\overline{X}$
75
RESTKÖRPER / REACTIVITY REST %
20
10
2σ
0

20
10
$\overline{X}$
0
REAKTIVITÄT STAUB / REACTIVITY DUST %
10
5
2σ
0

LUFTDURCHLÄSSIGKEIT / AIR PERMEABILITY nPm
16
8
4
2
1
0,5
0,250
0,125

0,20
0,10
% Na
0,00

0,04
0,02
% Ca
0,00

0,10
0,05
% Fe
0,00

0,04
0,02
% V
0,00

4,0
2,0
% S
0,0

BEZEICHNUNG / DESIGNATION

DATUM / DATE

├─┤ ENTSPRICHT ANODEN
EQUALS ANODES

VERFAHRENSENTWICKLUNG ELEKTRODEN SEPT. 81

ALUSUISSE
July 1979

C - 120 SAMPLING OF GREEN AND BAKED ANODES

1. Introduction

To know the quality of larger quantities of anodes, only relatively small samples can be used. The purpose of sampling and sample preparation is to use these samples for the required physical and chemical tests in such a way, that they correspond as far as possible to the quality of the total quantity. As the results of the tests represent the basis of important operational or economic decisions, maximum importance should be placed on the sample preparation.

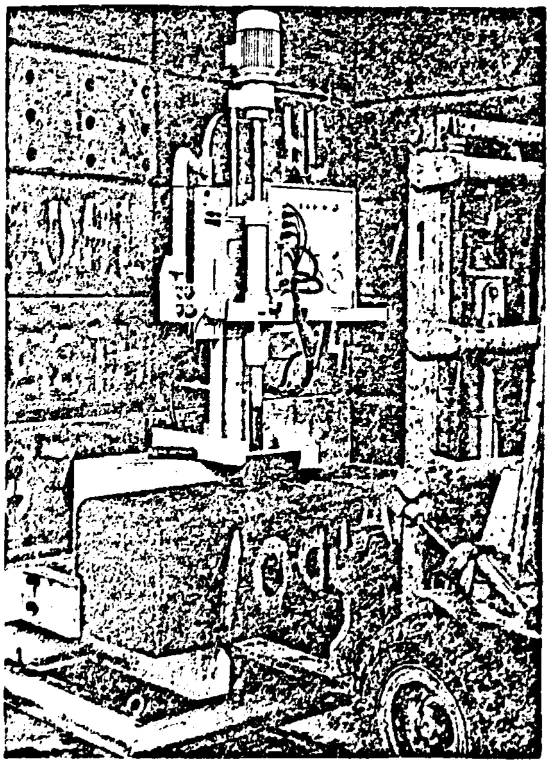
2. Methods

ALUSUISSE

3. Apparatus

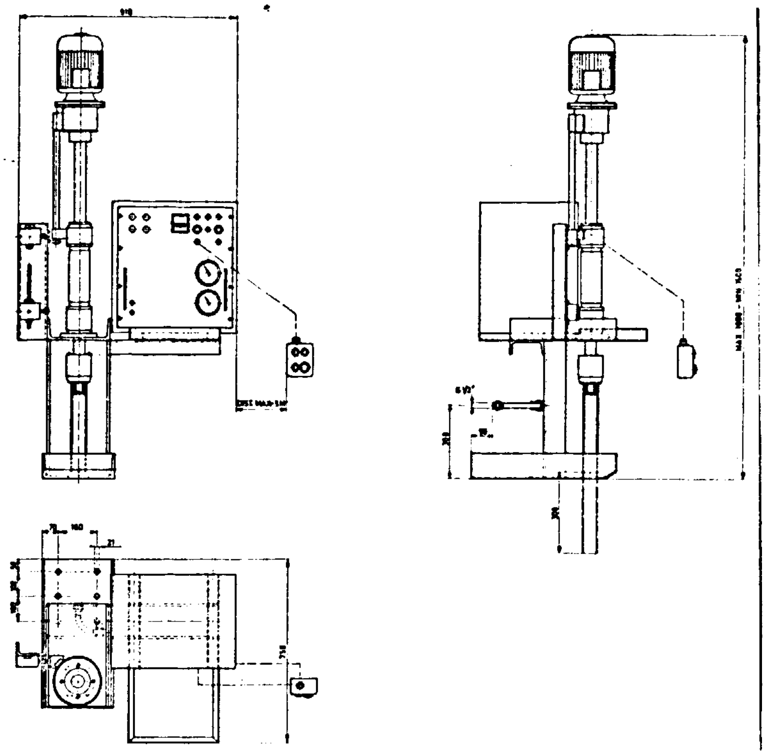
1 Core Drilling Machine Type-CDM

Capacity: 20 samples/hr.
El. connection: 3x380V/50Hz/1,5kW or 3x440V/60Hz/1,5kW
Revolutions: 1500 rpm
Travel: 300 mm
Spindle: 1¼"
Feed: hydraulic
Feeding force: 1000 N
Cooling of the core bit: water
Water consumption: 5-8 lt./min
Water connection: G ½"
Diamond core bit: ∅ 50/58 mm

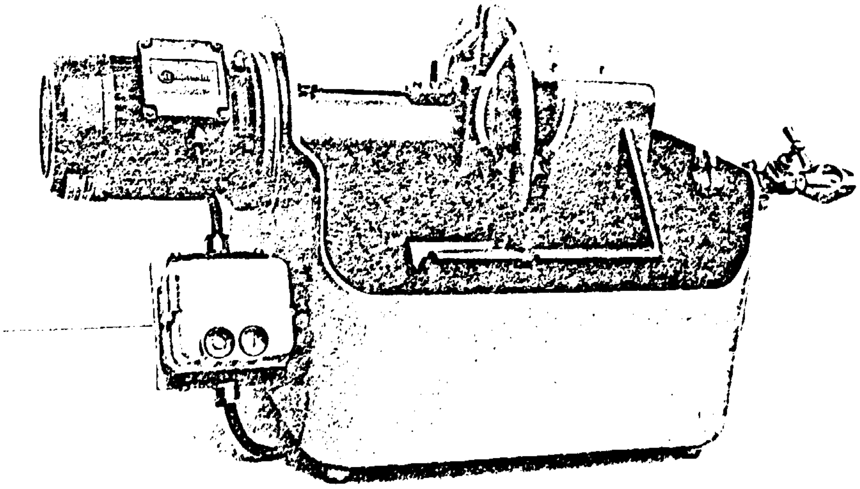


ALUSUISSE
July 1979
C - 120

Dimensions:



1 Diamond wheel saw Type DWC-250
Spare wheel: "Diamant Boart"
ϕ 250x1,50x10x25,0 mm



ALUSUISSE
July 1979
C - 120

Supplier of Core Drilling machine and Diamond wheel saw:

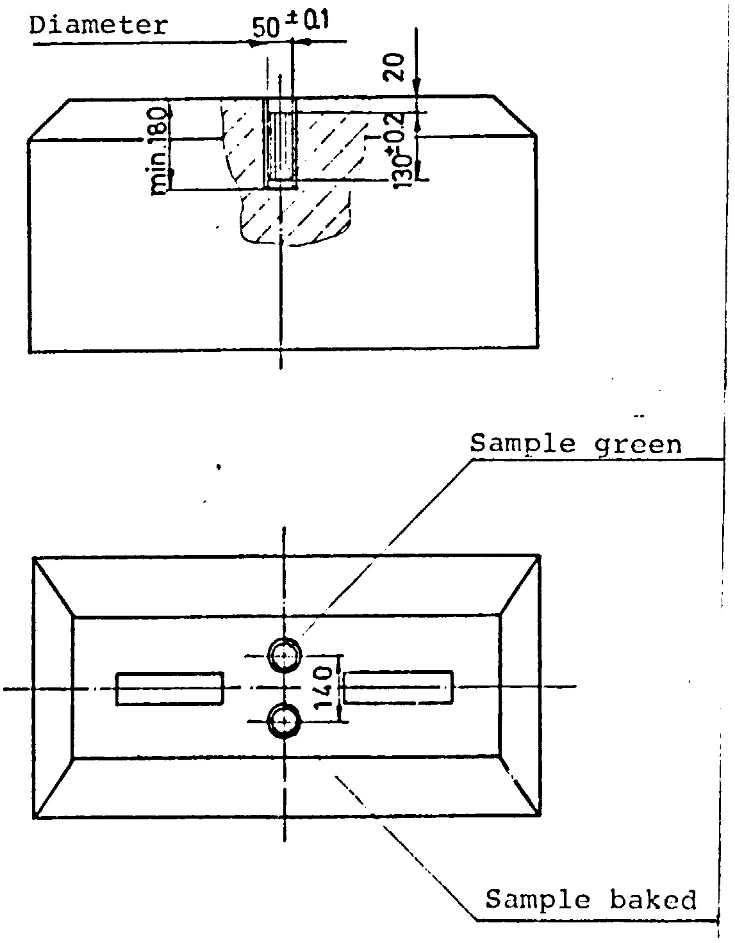
SWISS ALUMINIUM LTD.
Carbon Process Development
CH-3965 Chippis
Tel.: 027/57 11 01
Telex: 38 872

4. Sample

The sample is drilled 180 mm deep minimum. When using the apparatus which has been recommended, the following sample dimensions should be maintained:

diameter:	50 ± 0.1 mm
length baked:	130 ± 0.2 mm
face surfaces:	parallel

position:



ALUSUISSE
February 1979

C - 121

APPARENT DENSITY

1. Introduction

The measurement of the apparent density is a first indication of the quality of paste processing and of the anode characteristics to be expected.

2. Method

Determination of the density by weighing samples with standardised dimensions.

3. Apparatus

Balance with an accuracy of ± 0,1 g
Caliper

4. Sample

Carbon test cylinders

Length: L = 130 ± 0,2 mm
Diameter: d = 50 ± 0,1 mm
Condition: at 120 °C ± 2°C dried until weight remains constant

5. Execution of the Determination

The weight of the sample is determined with an accuracy of ± 0,1 g.

6. Evaluation and Accuracy of the Process

The apparent density is calculated as follows:

$$AD = \frac{G}{V} = \frac{G}{d^2\pi/4 \cdot L} \quad \text{in g/cm}^3$$

or for samples with standardised dimensions:

$$AD = \frac{G}{255}$$

where:

G = weight in g
d = diameter in cm
L = length in cm

The value determined is indicated to ± 0,01 g/cm^3.

Precision

Repeatibility: 0,01 g/cm^3
Reproducibility: 0,02 g/cm^3

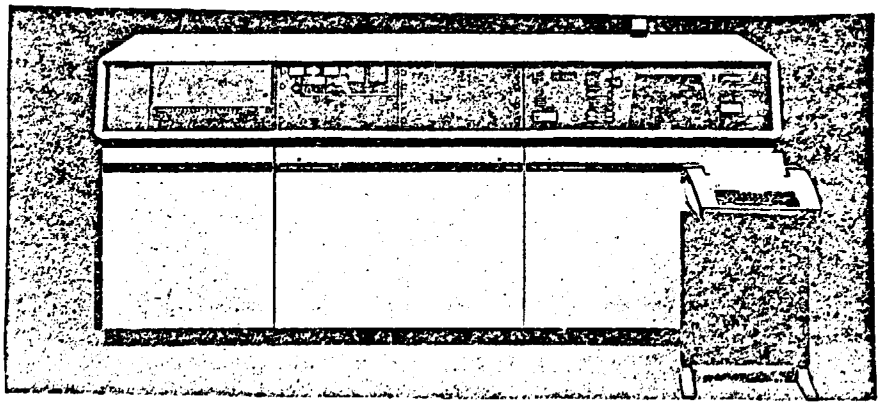
ALUSUISSE
October 1978

C - 124

DETERMINATION OF ELEMENTS

1. Introduction

Chemical analyses can be carried out in all laboratories of the Group by means of quantometers e.g. by using physical methods. The present method of examination is not concerned, therefore, with the equipment varying from one plant to another and its operation respectively calibration but with the production of the corresponding samples of coke, pitch, green paste and anodes.



X-Ray unit

2. Method

ALUCHEMIE Rotterdam

Aluchemie has been carrying out routine x-ray fluorescence ash analyses on anode materials for some years now. The experience thus gained was taken into account when this method of examination was developed.

3. Apparatus

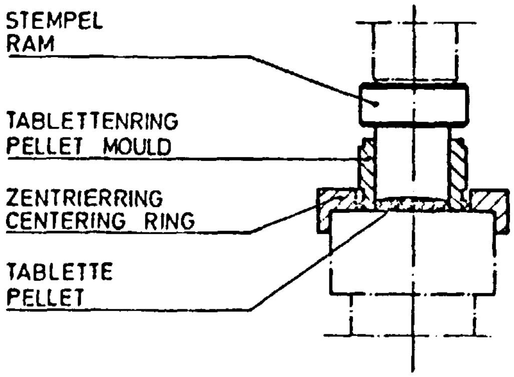
1 plate swinging mill with 100 cm^3 tungsten carbide milling container and pneumatic clamping device and automatic switch-off

1 tablet press: 20-40 tons with contact pressure gauge, time and press automatic (see page 3).

1 balance: 1000 g ± 1 g

1 pressing device

PRESSWERKZEUGE / PRESS TOOLS



Important: The dimensions of the ring moulds can be adapted to the sample of the different quantometer however, the tablet should have the following dimensions:

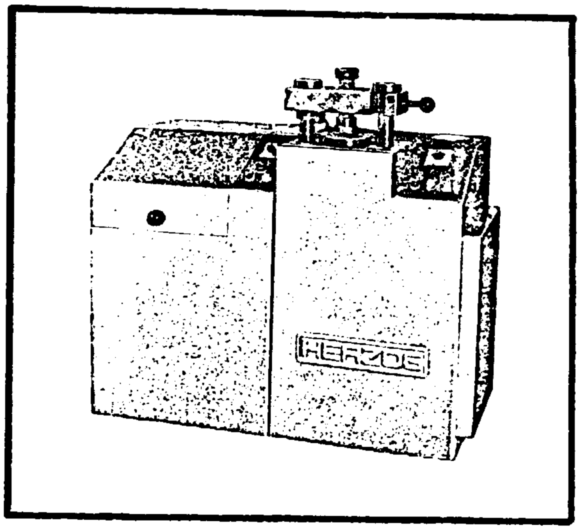
diameter:	approx.	30 - 40 mm
thickness:	approx.	4 - 6 mm

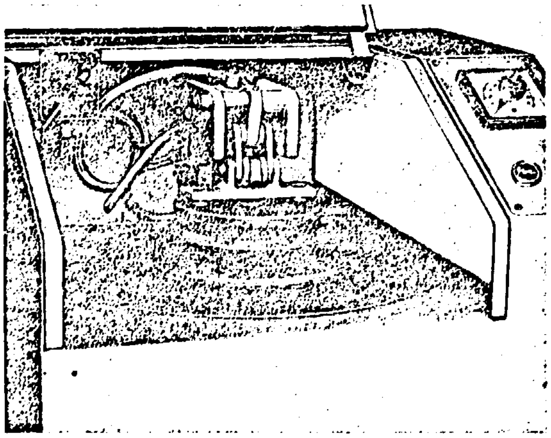
BESTIMMUNG DER ELEMENTE

DETERMINATION OF ELEMENTS

Schwingmühle HSM 100 mit
Tablettenpresse HTP 40

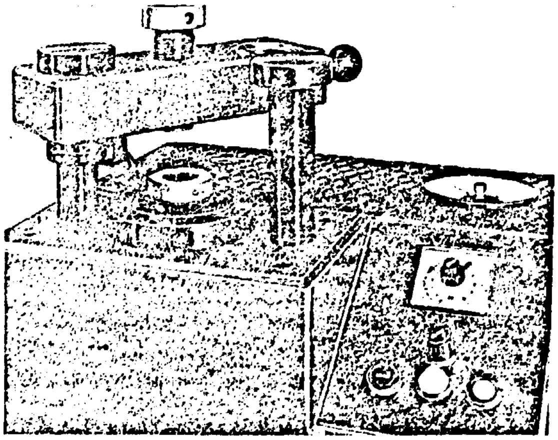
Plate swinging Mill HSM 100
with Pelletising Press HTP 40





HSM 100 mit Pressluft Haltevorrichtung für Mahlgefäss

HSM 100 with pneumatic clamping device for grinding container



HTP 40 mit Presswerkzeug

HTP 40 with fitted press tool

Stearine Acid: (granulated 1-2 mm) e.g. A 840 660 1005 by
UNILEVER - Emery
Bourtjy 1
GOUDA / NL

4. Samples

4.1 Coke

Quantity: 30 g ± 1 g

Granulometry: < 4,0 mm

Condition: dried at 120 °C until the weight remains constant. Oil treated coke heated at 400 °C, soaking time 12 h.
Green coke calcined in laboratory calcining furnace.

Processing: grinding time in plate swinging mill 60", addition of 5 g stearine acid, then an additional grinding time 30".

4.2 Pitch

Quantity: 30 g ± 1 g

Granulometry: crushed to 0,25 mm in the mortar.
No additional binder is required.

4.3 Green Paste and Søderberg Paste

Quantity: 30 g ± 1 g

Granulometry: < 4,0 mm

Processing: Grinding time in the plate swinging mill 60".
No additional binder is required.

4.4 Baked Anode Materials

Quantity:	30 g ± 1 g
Condition:	dried at 120 °C ± 10 °C to constant weight.
Processing:	as for 4.1 coke

5. Procedure of Determination

A sample of 30 g as stated in paragraph 4 is sufficient material for two tablets:

The centering ring is placed on the cleaned lower ram. A tablet ring mould is mounted in the opening into which half of the prepared sample (approx. 15g) is filled and then slightly pressed using the ram.

The press is switched on; the automatic pressing system is adjusted in such a way that the

maximum force of 10 tons

is applied on the tablet during 0.5 seconds. After pressing, the tablet ring is marked and kept protected against dust. Then the press is prepared for a new sample.

6. Evaluation, Accuracy of the Process

The following elements must be determined quantitatively in the electrode materials and stated as a percentage of the initial material:

	Na	Al	Si	S	Ca	Ti	V	Fe	Ni	Pb
coke	(x)			x	x		x	x	x	(x)
butts	x	x	x		x					
pitch	x			x	x					x
paste	x		x	x	x		x	x	x	x
anodes	x		x	x	x		x	x	x	x

(x) for pitch coke

A relative accuracy of 10% is sufficient. Details of repeatability and reproducibility are not yet available.

Total ash contents are only determined by way of exception and according to method **C - 125** according to a group internal agreement and are not calculated from the x-ray fluorescence results.

ALUSUISSE
October 1978

C - 126

SPECIFIC ELECTRICAL RESISTANCE

1. Introduction

The specific el. resistance of anodes is influented by raw material properties and production parameters. Large standard deviations may indicate irregularities during paste production or baking.

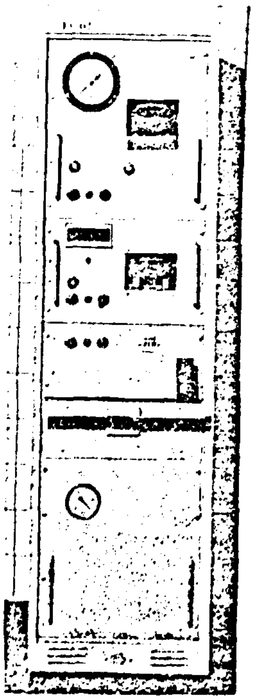
2. Method

ALUSUISSE Carbon Process Development

3. Apparatus

RESIFLEX 2

Apparatus for the determination of spec. el. resistance and flexural strength of anode samples.

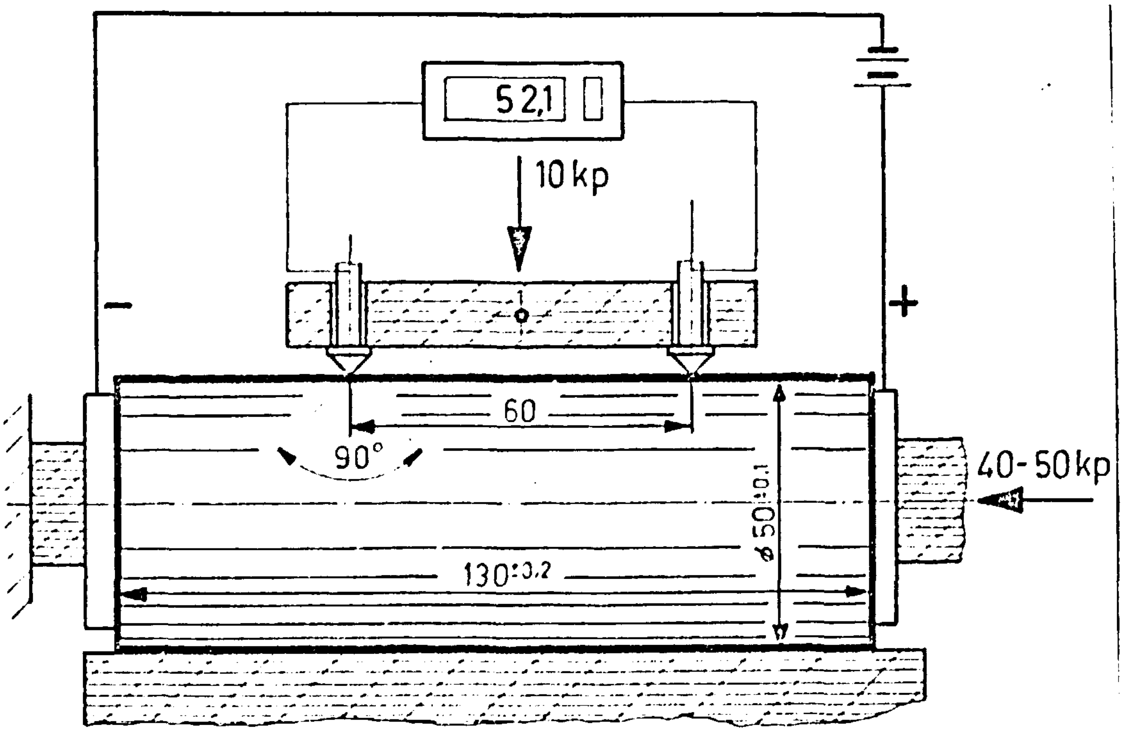


ALUSUISSE
October 1978

C - 126

Capacity:	30 samples/h
Dimensions:	see plan
El. connection:	3 x 380V, 50Hz/15 Amp. or 3 x 440V, 60Hz/15 Amp.
Weight:	ca. 120 kg
Sample dimensions:	l = 130 + 0,2 mm ⌀ = 50 + 0,1 mm
Supplier:	Swiss Aluminium Ltd. Carbon Process Development CH-3965 Chippis Tel.: 027/57 11 01 Telex: 38 872

Test arrangement:



4. Sample

Diameter:	50 ± 0,1 mm
Length:	130 ± 0,2 mm
Condition:	at 120 °C ± 2 °C dried until weight remains constant.

5. Procedure of Determination

The test apparatus is switched on ten minutes before the start of the measurements.

Calibration:

Before a series of measurements are taken, the equipment has to be checked with the standard. The digital mV-meter must show the value of the standard (calibration with potentiometer).

Execution of the determination:

The test cylinder is placed on the sample holder made of el. insulating material and hydraulically clamped.

The mV-meter reads the specific electric resistance of the cylinder. The measurements must be repeated at five different points of the cylinders.

6. Evaluation, Precision of the Procedure

The specific electrical resistance is the average value of five measurements.

The results are indicated to ± 0,1 $\mu\Omega$m (Ωmm^2/m).

Precision

Repeatibility:	1 $\mu\Omega$m
Reproducibility:	2 $\mu\Omega$m

ALUSUISSE
October 1978

C - 127

FLEXURAL STRENGTH

1. Introduction

In the case of a carbon specimen, Hook's law is not valid e.g. stress and strain are not proportional; Uni-axial force as applied in the compression test is not very suitable for the characterisation of these materials. The following test was developed to apply multi-axial forces on the samples.

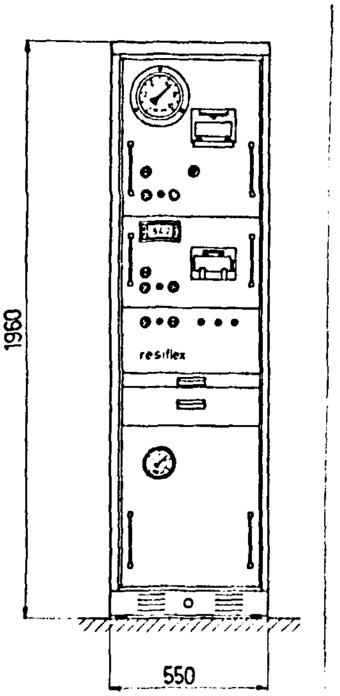
2. Method

ALUSUISSE Carbon Process Development

3. Apparatus

RESIFLEX 2

Apparatus for the determination of spec. el. Resistance and flexural strength of anode samples.



ALUSUISSE
October 1978

C - 127

Capacity: 30 samples/h

Dimensions: see plan

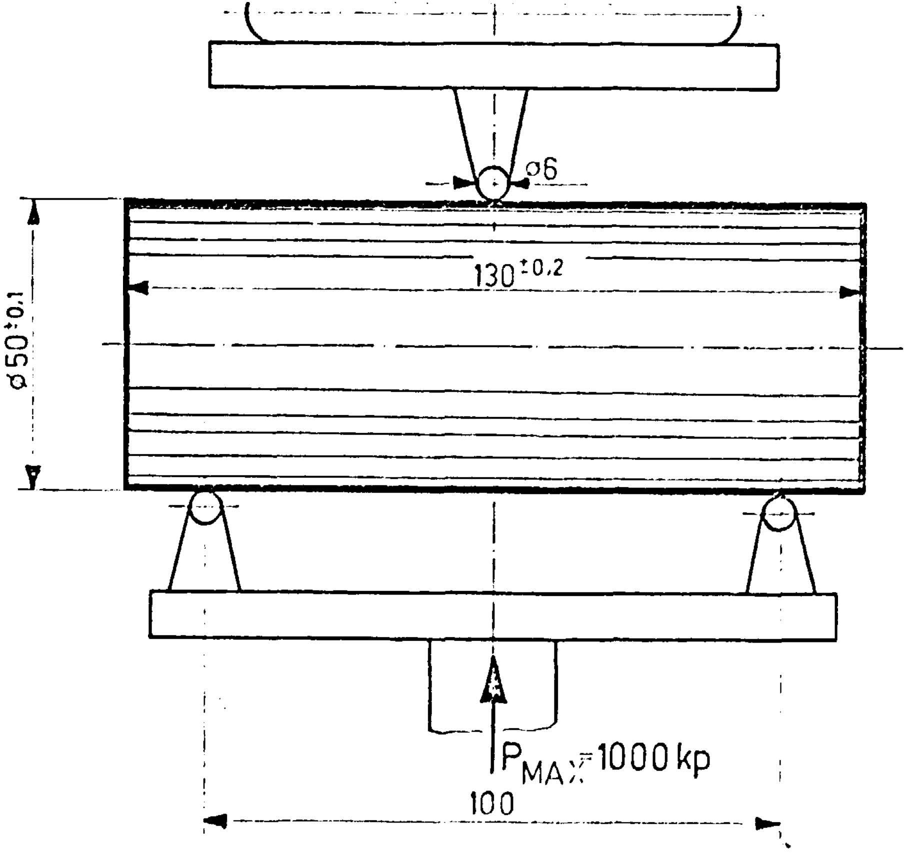
El. connection: 3 x 380V, 50Hz/15 Amp.
or
3 x 440V, 60Hz/15 Amp.

Weight: ca. 120 kg

Sample dimensions: l = 130 + 0,2 mm
ϕ = 50 + 0,1 mm

Supplier: Swiss Aluminium Ltd.
Carbon Process Development
CH-3965 Chippis
Tel.: 027/ 57 11 01
Telex: 38 872

Test arrangement:



4. Sample

Diameter: $50 \pm 0,1$ mm

Length: $130 + 0,2$ mm

Condition: at 120 °C ± 2 °C dried until weight remains constant.

5. Procedure of the Determination

The cylinder is placed on two supports and raised against a third one which is connected to a hydraulic pressure gauge. Using a valve the force can be slowly increased, until the sample will break. The breaking force is given in daN (~kp).

6. Evaluation, Precision of the Results

The flexural stress σ_B is calculated by the following formula:

$$\sigma_B = \frac{M_{max}}{W} = \frac{\frac{P \cdot 1}{4}}{\frac{\pi d^3}{32}} \text{ in daN/cm}^2$$

where

P = breaking force in daN

1 = distance between supports = 10 cm

d sample diameter: $5,0 \pm 0,01$ cm

By using these constant dimensions

$$\sigma_B = P \cdot 0,204$$

P = reading in daN

The value obtained is calculated in daN/cm^2.

Precision

Reproducibility: 5% rel.
(between average values of min. 30 samples).

ALUSUISSE
October 1978

C - 128

REACTIVITY TEST OF CYLINDERS

1. Introduction

Carbon reacts with carbon dioxide according to the equation

$$CO_2 + C = 2\ CO$$

The loss of anode material by the reaction with CO_2 which arises in certain constant conditions, and the weights of the remaining specimen and of the material loss are of importance for the prediction of the later behaviour of the anodes in the electrolysis.

2. Method

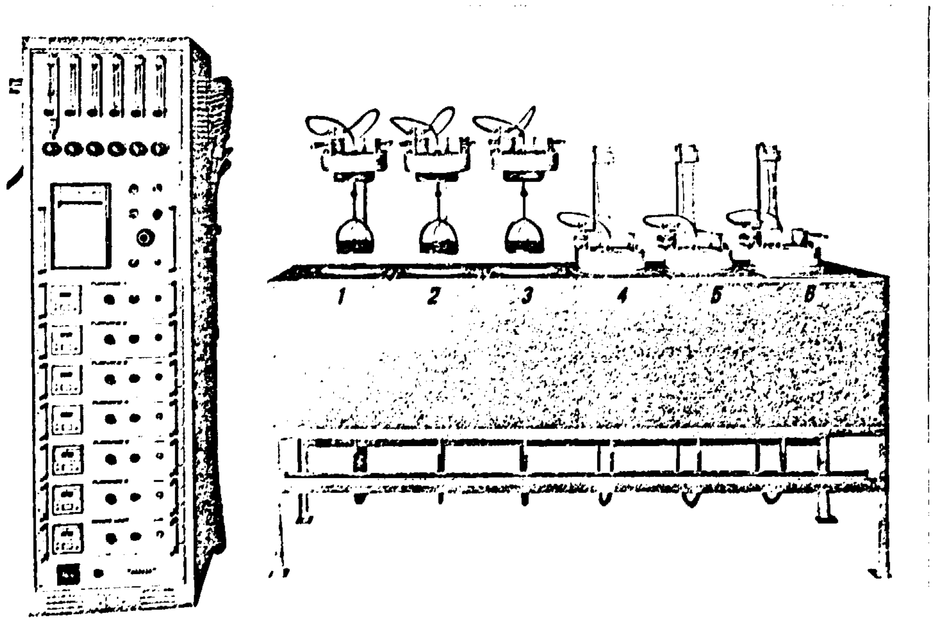
ALUSUISSE Carbon Process Development

A baked test cylinder is subjected to a constant CO_2-flow for 7 hours at 960 °C.

3. Apparatus

R 6-automat

Apparatus for the determination of the burning behaviour of anodes.

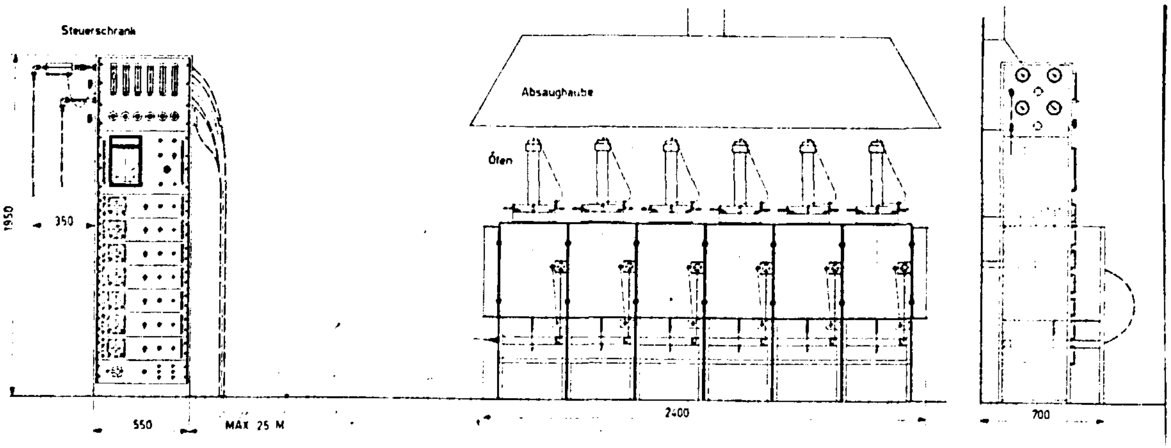


ALUSUISSE
October 1978

C - 128

Capacity:	24 samples/day
Dimensions:	see plan
Furnaces:	6
Temperature:	960 ± 2 °C
Weight:	600 kg
El. connection:	3 x 380 V/50Hz/25 Amps or 3 x 440 V/60Hz/25 Amps
Gas consumption:	CO_2: 2 kg/sample N_2 : 0,6 Nm^3/sample

Dimensions:

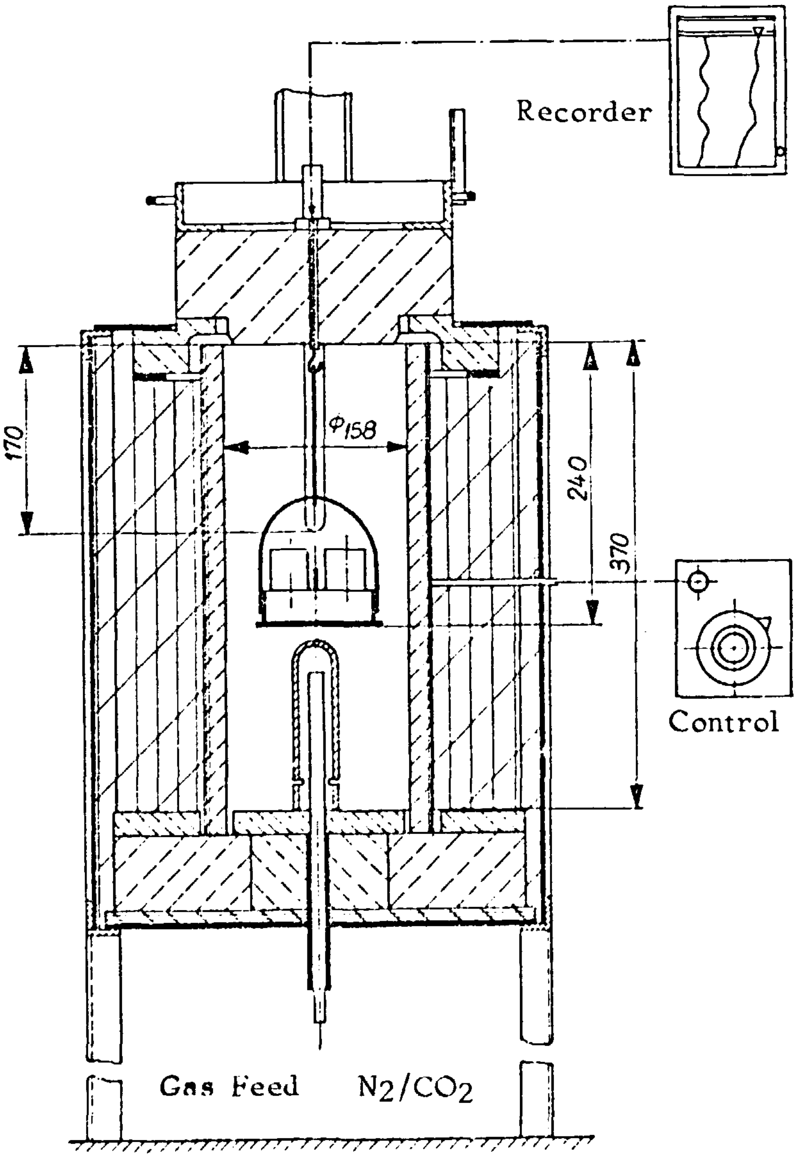


Supplier:

SWISS ALUMINIUM LTD.
Carbon Process Development
CH-3965 Chippis
Tel.: 027/57 11 01
Telex: 38 872

In a muffle furnace with the measurments stated on page 3,the temperature is kept constant at 960 °C ± 2 °C. In the center of the muffle two test specimens stand on a plate of heat resistant steel.

By means of thermoelement and recorder the temperature 1 cm above the samples is registered. N_2 or CO_2 can be introduced into the muffle. The quantity during the duration of the test must not deviate more than ± 3%. After the test, the rest of the specimen is put into a tumbling apparatus and mechanically tumbled with steel balls for 20 minutes.



Furnace

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October 1978

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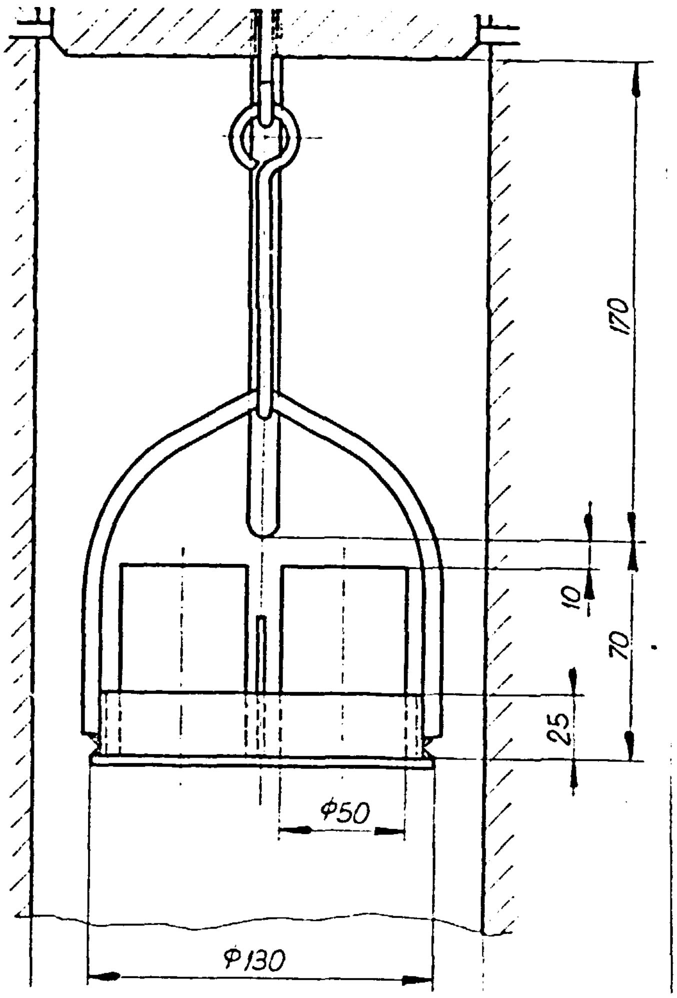
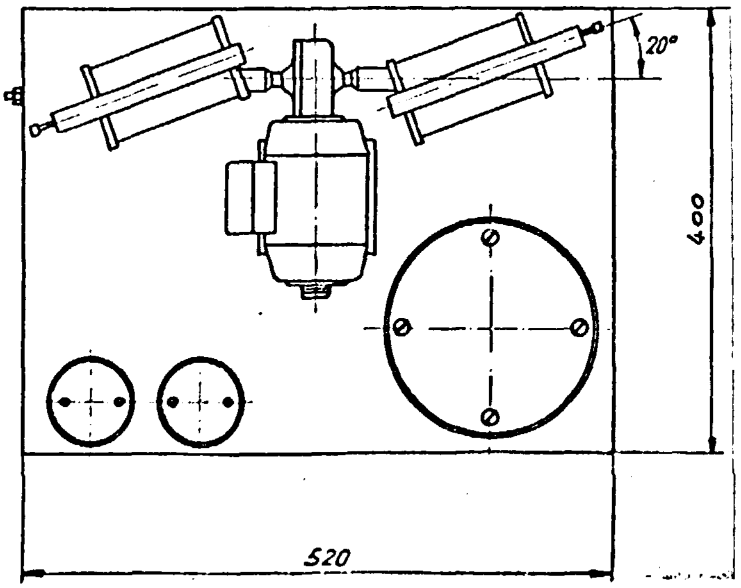


Position of the Samples and the Thermo-Element



Tumbling Apparatus

Milling Container:

Length: 120 mm, internal diameter: 62 mm

Balls: Material: Steel 50 pieces ϕ 6 mm

Revolutions: Total 3600 at max. 160 rpm

Balance:	1000 g	Accuracy:	± 0.1 g
Gas: CO_2:	better than 99.5%, $N_2 + Ar < 0.5\%$ $H_2O < 150$ mg/Nm^3	N_2:	better than 99.5%; $O_2 < 0.5\%$ $H_2O < 60$ mg/Nm^3

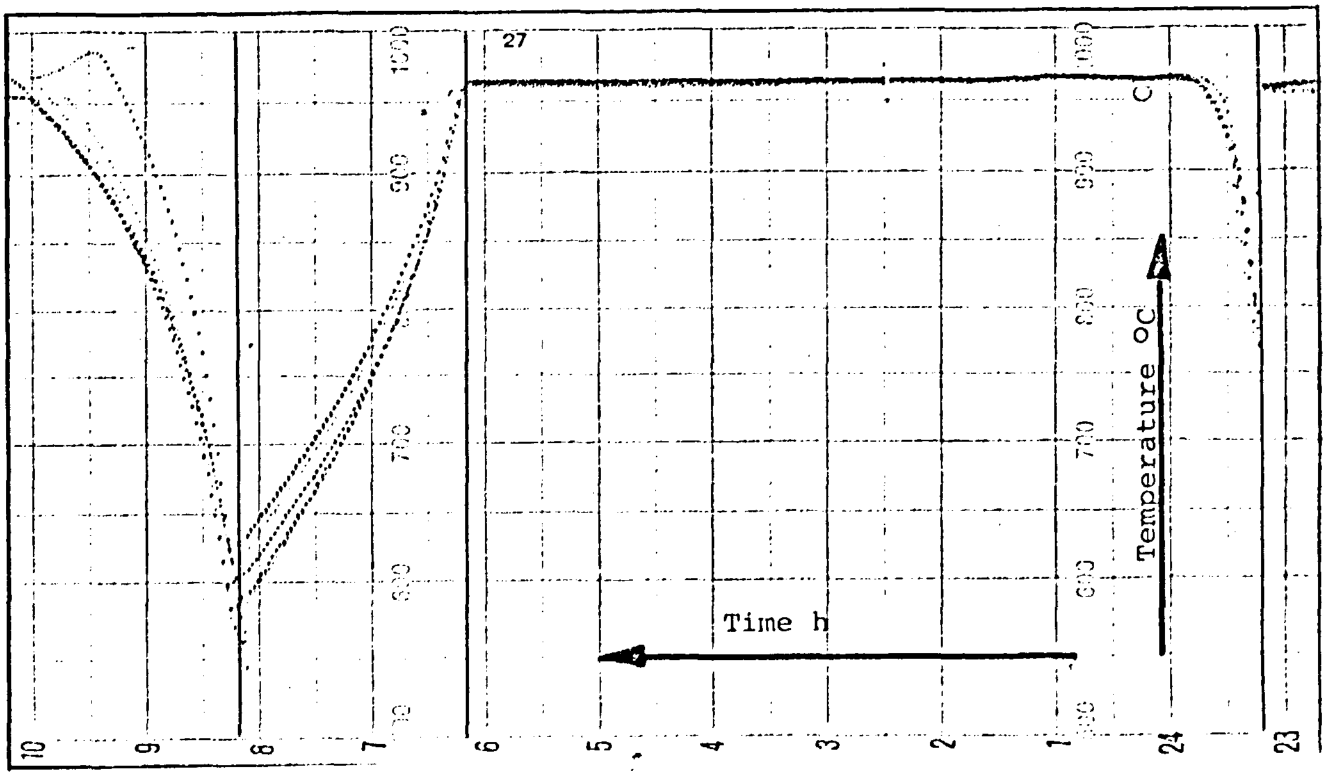
4. Sample

After determining the flexibility strength, the following sample is made from one remaining half of the cylinder.

Diameter:	d = 50 ± 0.1 mm
Length:	L = 60 ± 5 mm
Condition:	dried at 120 ± 2 °C until weight remains constant

5. Execution of the Determination

One hour before charging the samples (time 0) N_2 is introduced into the furnace.



At time 1 the sample plate is hooked on at the furnace cover and the gas feed changed to CO_2. The gas quantity amounts to 350 l/h (rotameter reading). After 7 hours (time 8) the furnace is switched off and the gas feed changed to N_2 with the same rotameter adjustment. The temperature in the switched-off furnace drops to 600 °C-550 °C. After two hours (time 10) the samples are taken out, the gas feed stopped and the furnace switched on again.
After two additional hours (time 12) the temperature of the furnace is between 965 °C and 975 °C whereupon N2 is introduced again and after 1 hour (time 13) the next samples are loaded. The required temperature is automatically achieved again. Once the sample has cooled down to room temperature in the air, they are tumbled in the corresponding apparatus. The following weights are determined:

- material detached and fallen down to the sample plate by selective burning in the furnace and material detached by tumbling = m_1.
- residual body = m_2

Notes:

The times and temperatures can be seen from the diagram on page 5 , and important is to achieve a certain heating and cooling rate.

Possible deviations in temperature shall be corrected one hour (time) after loading of the samples.

Small constant deviations from the required gas quantity (up to ± 50 lt/hr) shall only be corrected when the furnace is empty, as it only has little influence on the examining result. Slowly changing deviations on the other hand can give a completely false picture as the temperature in the furnace begins to deviate and therefore, have to be avoided (e.g. change of gas bottle in time).

The inside temperature of the furnace has to be measured once a week with a calibrated thermoelement with an instrument with digital indication and must coincide with the value indicated on the recorder.

Maintenance of the geometrical conditions according to page 3 shall be checked each month.

The required temperature precision of ± 2 °C can be maintained with the apparatus R-6 Automatic/R-12 Automatic (see diagram on page 5).

6. Evaluation, Precision of the Determination

m_o = weight of sample (g)	= 100 (%)
m_1 = detached (g)	$= \frac{m_1}{m_o} \cdot 100$ (%)
m_2 = residual body (g)	$= \frac{m_2}{m_o} \cdot 100$ (%)
Δm = reactivity $= m_o - (m_1 + m_2)$ (g)	$= \frac{\Delta m}{m_o} \cdot 100$ (%)

The values are given ± 0.1 %.

Precision

Repeatibility: Residual body m_2 = 2% abs.
Reproducibility: Residual body m_2 = 4% abs.

ALUSUISSE
October 1978

C - 111

DENSITY IN XYLENE

1. Introduction

The density in Xylene (formerly "true density") is a specific material property and gives rise to conclusions as to coke-quality and calcination degree.

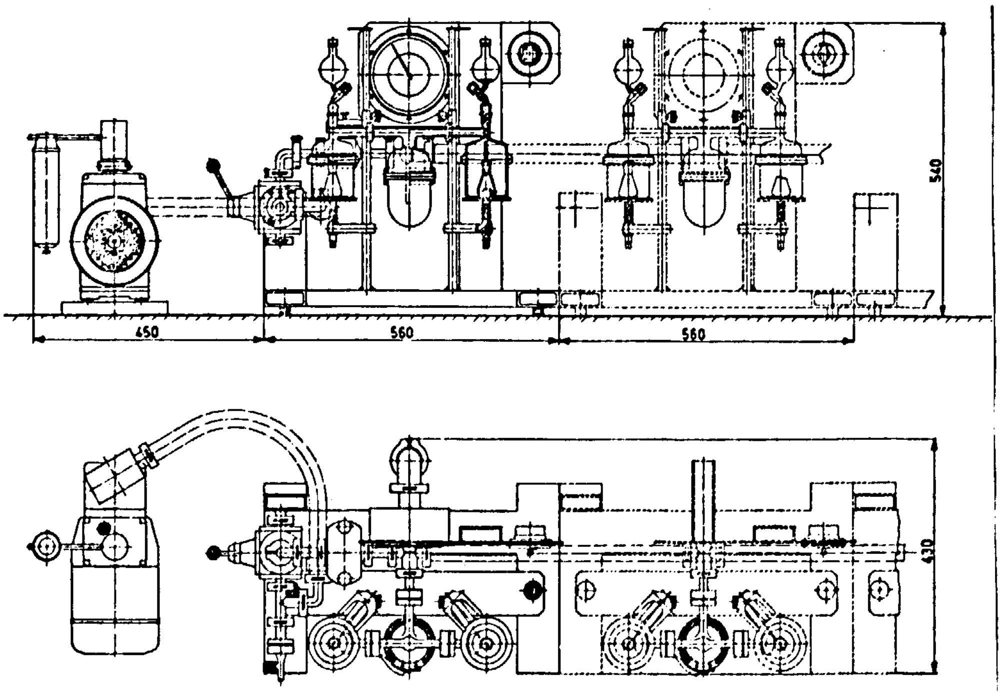
2. Method

ALUSUISSE Carbon Process Development
Determination of the density in vacuum by means of pycnometer.

3. Apparatus

1 ALUSUISSE Apparatus for the determination of the density of coke and powder

Dimensions:



ALUSUISSE
October 1978

C - 111

Weight: 25 kg

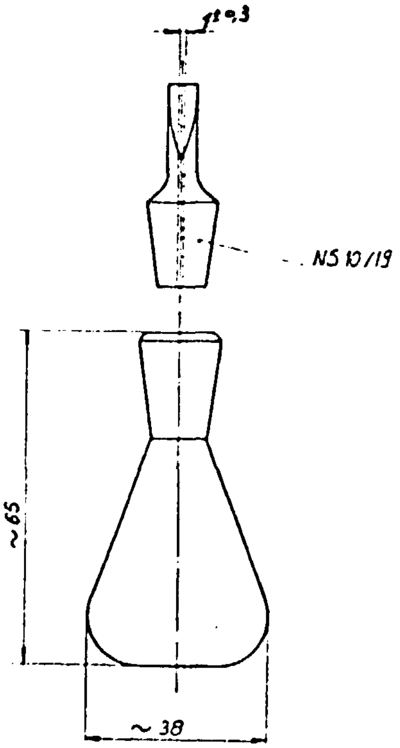
El. Connection: 220V/50/60Hz/200 W

Pressure: 1-100 mbar

Supplier: SWISS ALUMINIUM LTD.
Carbon Process Development
CH-3965 Chippis
Tel.: 027/57 11 01
Telex: 38 872

10 Pyknometer 25 ml
Gay Lussac
Nr. 433 20

Supplier: BRAND Rudolf
Ferd. Friedrichstr.
BRD-6980 Wertheim 2
Tel.: 09342/813137
Telex: 689 110



1 drying oven: content 50 lt, temperature 120 ± 2 °C

1 thermostat: content approx. 10 lt, opening diameter 12 cm. Bath with grid, temperature constancy at 25 °C better than ± 0,05 °C.

Recommended: circulation thermostat Type TE 9-50

Supplier: P.M. TAMSON N.V.
Zoetermeer/Holland

3 1-litre spray bottles with Xylene commercial grade
with distilled water (boiled)
with Acetone

2	desiccators, diameter 30 cm
2	desiccators, diameter 15 cm
10	glass beakers, 200 ml
10	glass beakers, 150 ml
1	analytical balance, max. load: 200 g, sensitivity 0.0001 g
1	hand vibrator with filling device, e.g. Mettler Type LV2
1	detergent, e.g. Ajax

4. Sample

Sample weight: 5 g ± 0.1 g

Grain size: 95% < 0.063 mm, completely grounded

Condition: dried at 120 ± 10 °C min. 8 hours, then cooled in the desiccator and stored.

5. Execution of the Determination

5.1 Calibration of the Pycnometers

Pycnometers in normal commercial use are calibrated at 20 °C. A conversion to testing temperature is generally not possible. The volume of the pycnometer is, therefore, determined with distilled water. It is filled with water of approx. 23-24 °C, the ground stopper inserted firmly and the pycnometer cleaned from excess water with filter paper.

The pycnometer is brought into the thermostat and heated to a temperature of 25 ± 0.05 °C. During warming the liquid which leaves the capillary bore should be removed carefully with filter paper. If no water runs out any more, the pycnometer has reached the test temperature. It is taken from the thermostat and dried carefully. To avoid running over due to temp. of the hand, brief chilling in cooler water or with Acetone can take place beforehand. The pycnometer which is completely dry on the outside is weighed exactly on the analytical balance to ± 0.0001 g.

$$\text{Volume } V_o = \frac{m_{\text{tot W}} - m_o}{0{,}99705} \quad (\text{cm}^3)$$

The determination of the content = "Volume V_o" should be carried out several times on different days to eliminate weather influence and a slightly different adjustment of the thermostat. The Volume V_o is the mean value from 8-10 determinations. However, the individual values should not deviate from the mean value by more than ± 0.0015 cm^3. Pycnometers which supply greater dispersions, are unsuitable for an exact determination. The volume of the pycnometer is given rounded of to 0,001 cm^3. Calibration should be repeated in quarterly to semi-annual periods. Changes of the Volume V_o within this period should be recognized among other things from the empty value which should be found constant at ± 0.001 g.

5.2 Determination of the Xylene Density (Density Ration)

For the determination normal commercial Xylene can be used (e.g. Xylene p.A. by Merck). As described in 5.1, the pycnometer is filled with Xylene, kept in the thermostat at 25 ± 0.05 °C and the density of 25 °C of Xylene is calculated.

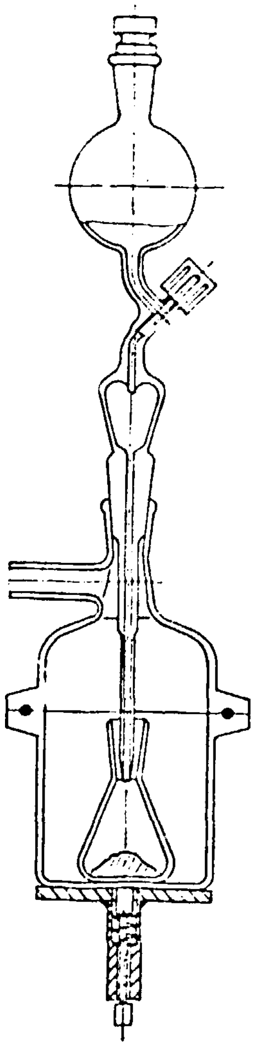
$$\delta_{Xy} = \frac{m_{tot\ Xy} - m_o}{V_o} \quad (g/cm^3)$$

The determination of δ_{Xy} should be repeated several times, if possible on different days. The density is determined at exactly ± 0.0001 (g/cm3); the Xylene value is the mean value from several determinations. The deviation with pycnometers exactly calibrated is not greater than ± 0.0001 g/cm^3. If greater difference arise, the pycnometers which give greater variations in values, should not be used.

5.3 Execution of the Actual Determination

Per sample according to paragraph 4, two determinations should be carried out. Approx. 5 g of the sample are weighed into the dry, clean pycnometer. The pycnometer with its contents is placed into the device which permits an evacuation with simultaneous feeding of Xylene.

Before adding Xylene, for a short period (15 min), evacuation is carried out at a pressure of 10 ± 2 mbar with the Xylene feed closed. Thereafter Xylene is added in drops to the pycnometer. Too rapid filling should be avoided. After the substance in the pycnometer is covered with max. 20 mm Xylene, the addition of Xylene is interrupted. The evacuation is continued until the evaluation of air bubbles has stopped. From time to time the pycnometer is shaken to facilitate this.



In general, after 60 minutes the sample is free of air. After filling the apparatus with air, the pycnometer can be removed. Then the pycnometer is filled with Xylene to the lower edge of the ground section. After the solid material has settled (at least 30 minutes), the pycnometer is filled to the edge and the ground-in stopper with the capillary bore carefully applied. Further treatment e.g. tempering to 25 °C takes place as described in 5.1.

By weighing the pycnometer, the weights of the sample and of Xylene added, is determined. The density of the solid substance can be calculated from the Volume V_o and the above mentioned values.

6. Evaluation, Precision of the Procedure

6.1 Measuring Sheet

δ_{Xy} 25°C = 0.8________ g/cm^3

Date:__________ Room Temperature:__________ °C Laboratory Assistant:__________

1 Pycnometer No.		
6 $m_{tot} = m_o + m_{Xy} + m_C$ 4 $m_o + m_C$		
3 m_o		
5 $m_C = (m_o + m_C) - m_o$ 7 $m_{Xy} = m_{tot} - (m_o + m_C)$		
2 V_o $V_{Xy} = m_{Xy}/\delta_{Xy}$		
$V_C = V_o V_{Xy}$		
$d_{Xy} = m_C/V_C$		

m_o:	weight of pycnometer (g)
m_{Xy}:	weight of Xylene (g)
m_C:	weight of sample (g)
δ_{Xy}:	density of Xylene
V_o:	volume of pycnometer (cm^3)
V_{Xy}:	volume of Xylene (cm^3)
V_C:	volume of sample (cm^3)
d_{Xy}:	density of sample in Xylene

6.2 Precision

Repeatability (one observer, one instrument)
0.004 g/cm^3.

Reproducibility (various observers and instruments)
0.006 g/cm^3.

The result is roundet off to the third point and stated.

6.3 Control

Systematic errors can be recognized by including a control sample. If the result of the control samples deviates by more than 0.004 (mean value between two determinations) from a value determined over a longer period of time, all determinations shall be repeated after checking the experimental conditions.

Alesa Alusuisse Engineering, Ltd.

ANNEX 7

Application of Pilot Plant Work in Prebaked Anode Manufacturing

APPLICATION OF PILOT PLANT WORK IN PREBAKED ANODE MANUFACTURING

Dr. A. Odok, W.K.Fischer

Summary

When new raw materials are introduced for the fabrication of prebaked anodes, it is still very problematic to predict the quality of the resulting anodes. The scientific and technological knowledge available today is by no means sufficient to enable the design of process practices without actual experimentation.

In ALUSUISSE this experimentation is conducted in a Pilot Plant where small anodes (4 to 8 kg), which in all aspects duplicate the properties of production anodes, are used. The pilot plant is described and its utilization to solve various types of problems encountered in prebake anode production is illustrated through examples.

AIME 1978, p. 269

Introduction

Process development in the prebaked anode plants is difficult: the size of the installations and the very nature of the process itself dictate a very cautious approach towards changes. A minute change in recipe or baking practice can have a major influence on anode quality and even lead to enormous quantities of reject. The potential costs involved in making development directly in the fabricating plants has always been a limitation for the experimentation with this process. It is not to say that the need for optimisation of the process does not exist but the risk incurred has always circumscribed the progresses. This risk can be in great part eliminated when the development work is conducted on a pilot plant scale. The changes successfully tested at low cost in the pilot plant, can be safely introduced in the fabricating plant as long as the pilot process and samples duplicate adequately the full-scale operations and products.

The use of test anodes of small dimension to study problems such as the correlation between material properties and anode quality (1,5), the optimisation of aggregate size distribution (6, 9), the technical assessment of new process steps (10-11), has been abundantly described in the literature. Nevertheless such pilot plant studies appear to have remained restricted to well defined specific technical points. At ALUSUISSE, the utilization of pilot plants is generalized, all the major anodes plants are equipped with such units. As a result of a continuous development effort, it has been possible to reach a stage whereby test anodes of small size duplicate in all aspects the full sized anodes produced on the production lines. These pilot plants have become even more indispensable since the oil crisis. The anode plants are presently almost continuously compelled to use raw materials with very different physical and chemical properties. To respond to this situation, pilot plants are used in three ways:

1. selection of raw materials available on the market (cokes and pitches)

2. optimisation of dry aggregate mixture and binder combinations

3. design of production practices for these various formulations.

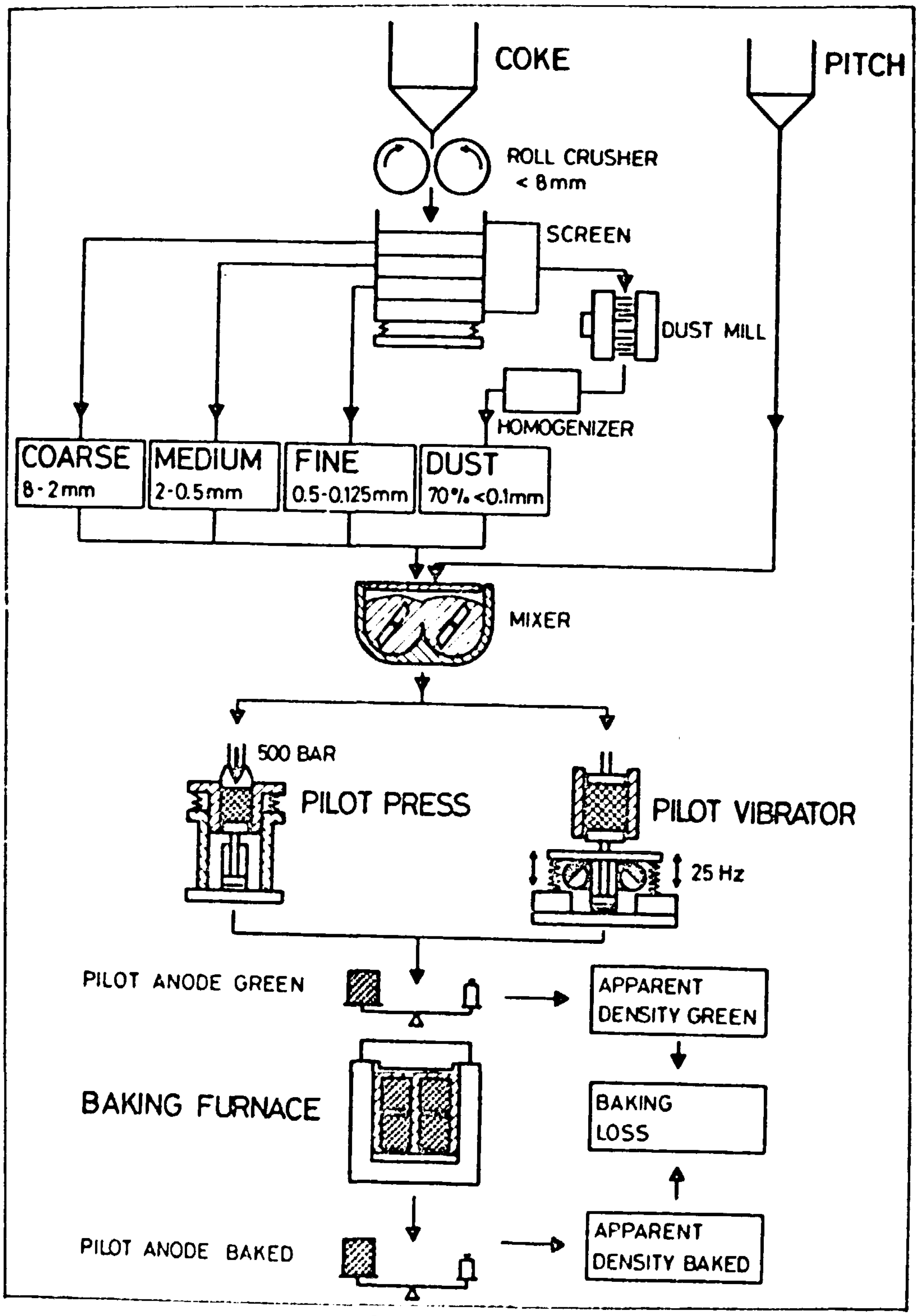


FIG. 2

Process Flow Sheet of the Pilot Plant

Description of the Pilot Plant

The test anodes from the pilot plant are scaled down to 1/100 of the size of the anodes produced on the production lines (Fig. 1).

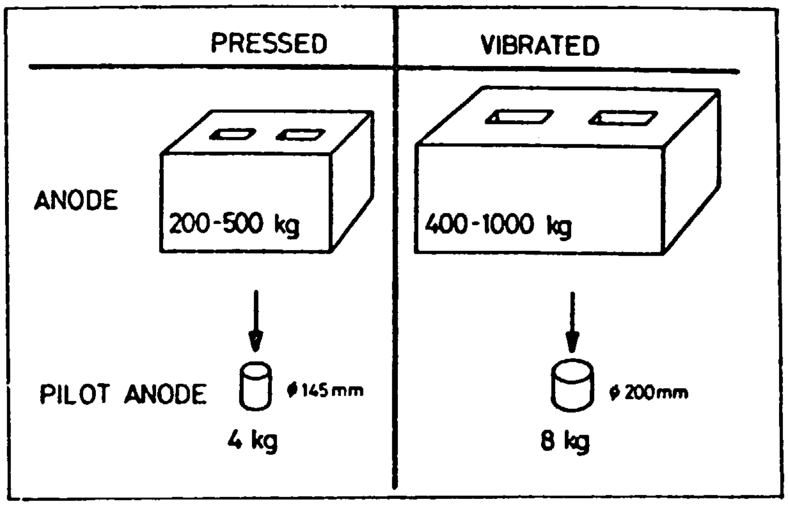


FIG.1

Fig. 2 shows the process flow for the pilot plant.

a) Production of the green paste: The dry material is ground and separated into three fractions: 8-2 mm, 2-0.5 mm, 0.5-0.125 mm. Fractions outside the range 8-0.125 mm are processed into dust through a laboratory crossbeater mill into the desired fineness. The size distribution of the dry aggregates in the pilot plant is the same as the one used on the production lines. 60 kg of dry mixture are heated up to 200°C in a 100-liter sigma blade mixer. Solid pitch is then added and mixed for 20 minutes at a temperature 60°C higher than its Mettler softening point (ASTM-D 3104-72).

b) Forming and baking: The green paste is either pressed or vibrated under the following conditions:

pressed anodes 20°C above softening point at a pressure of 500 bar.

vibrated anodes 40°C above softening point at a vibrating frequency of 25 Hz and an amplitude of 3-4 mm.

Fig. 3 and 4 show respectively the types of press and vibrator used.

The test anodes are baked in an electrical furnace (25 kW) using petrol coke (-2 mm) as packing material. The heating cycle is programmed to a maximum temperature of 1200°C. The apparent density is measured before and after baking so that the losses incurred during baking can be calculated.

Properties of Test Anodes

From each baked test anode, two or three cylinders 50 ± 0.1 mm in diameter are extracted with a core drill and cut to an exact length of 103 ± 0.2 mm with a diamond wheel saw.

The measurement of the physical and chemical properties is performed on 24 such cylinders. Fig. 5 illustrates the test program:

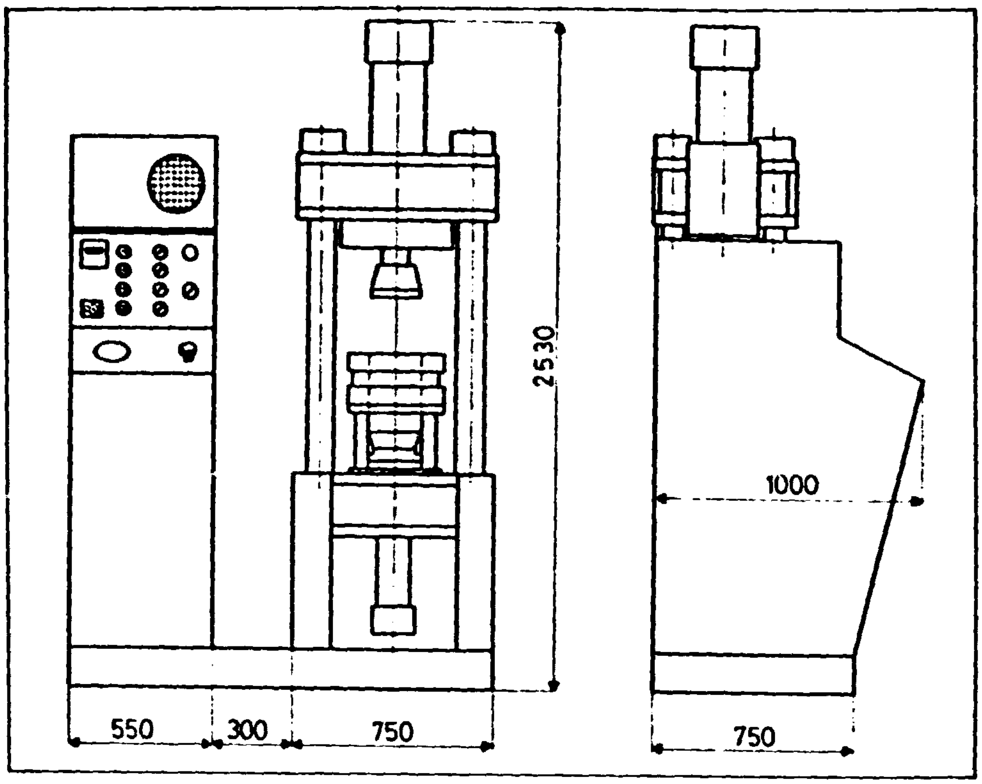
- apparent density
- specific electrical resistance
- flexural strength
- carboxyreactivity
- chemical elements.

This test program is the same as the one being performed routinely to control the quality of the full sized anode from the production line (Fig. 13 and 14).

The relationship between the properties measured and the behaviour of the anodes in the electrolytic cell have been already described (12-13). The following relationship between measured reactivity and the net anode consumption has been statistically established from test data with large current intensity reduction cells:

$$\boxed{\begin{array}{c}\text{Net anode consumption}\\ (\text{g/kg Al}) = 444+330 \times \text{dust in } \%\end{array}}$$

To sum it up, it is possible to fabricate in the pilot plant, test anodes whose properties are similar to the ones of the full sized anodes from the production lines and also to predict from the measured properties their behaviour in the electrolytic cells.



Pilot Press FIG. 3

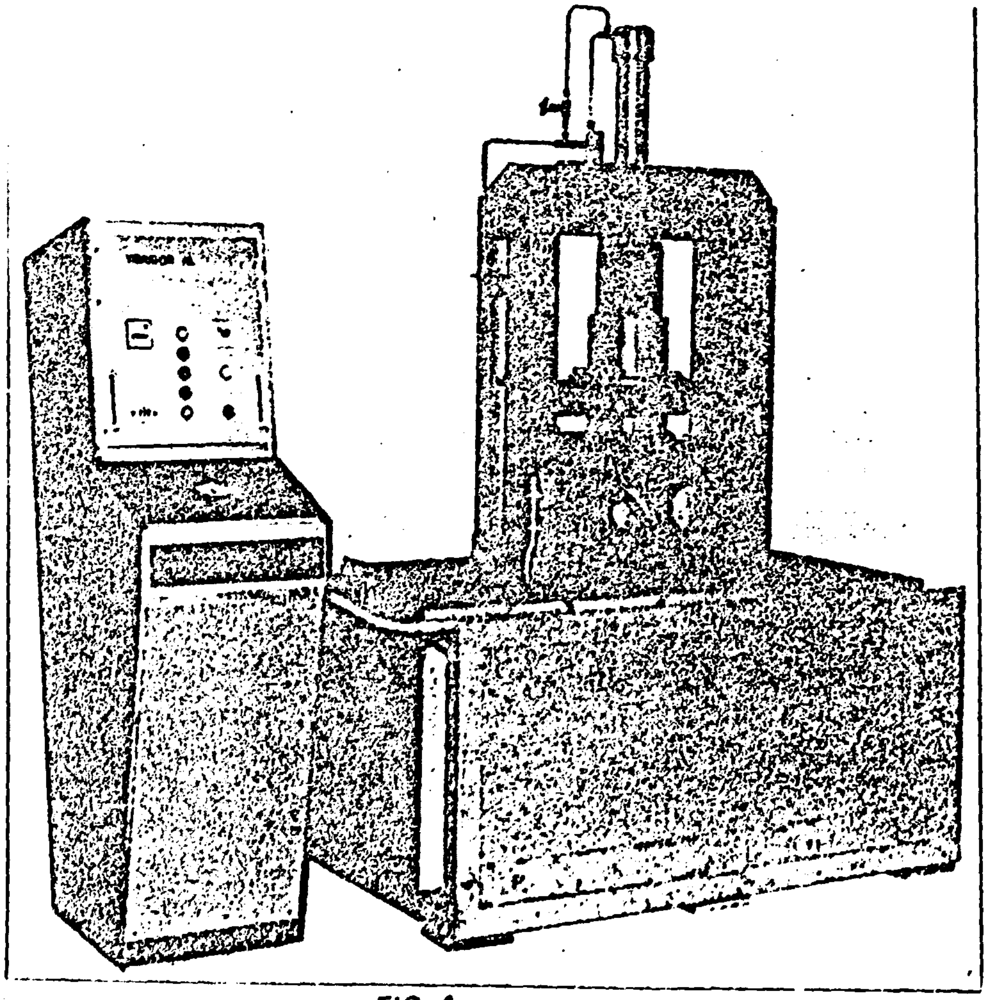


FIG. 4

Pilot Vibrator

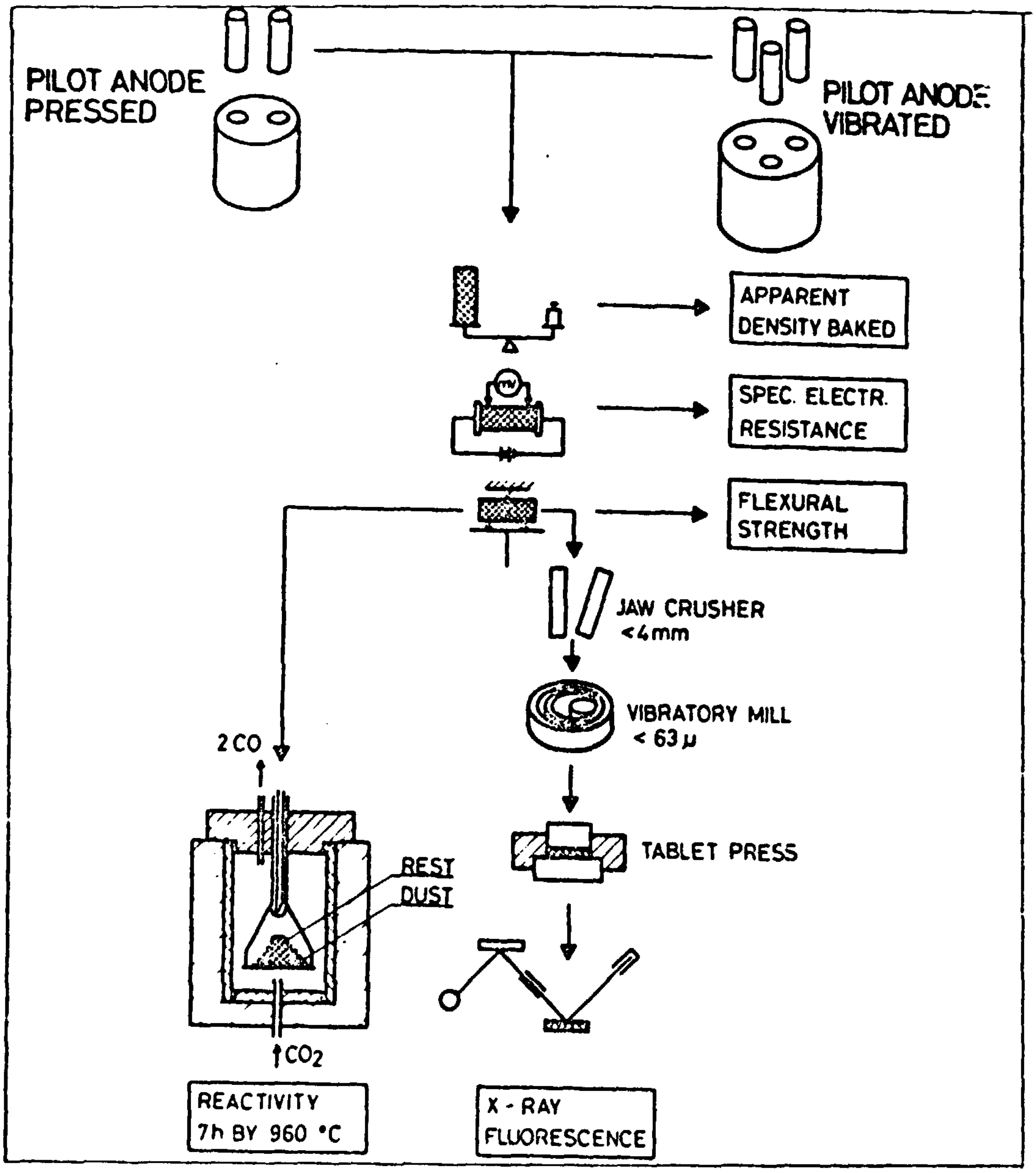
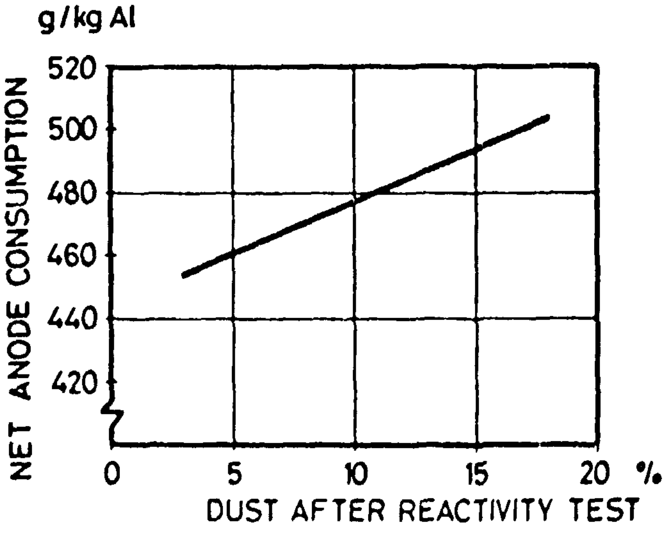


FIG.5

Schedule for testing baked Pilot Anodes



Correlation between net Carbon Consumption and Dust after the Carboxyreactivity Test

FIG.6

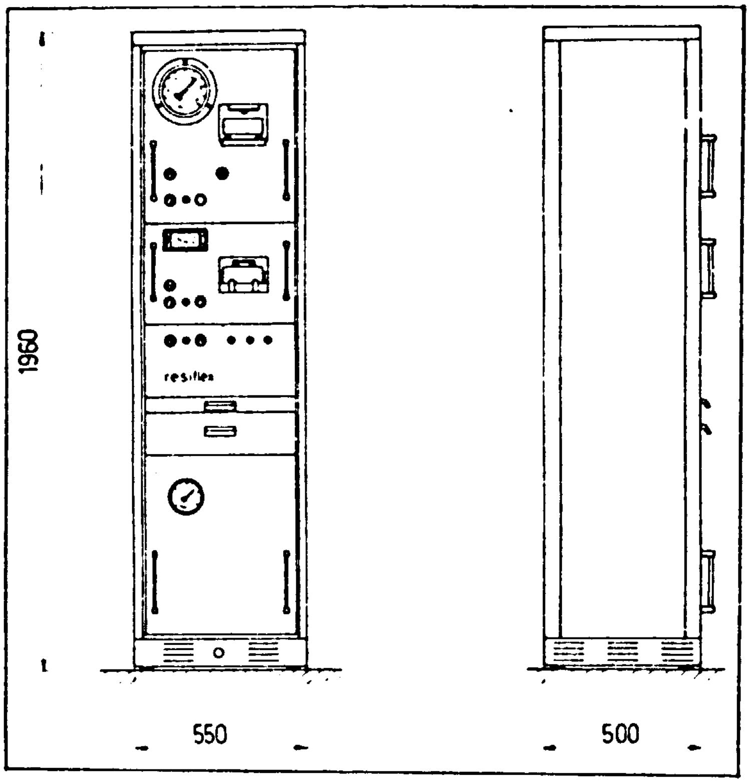


Fig. 13

Resiflex 2

Apparatus for the determination of spec. electrical resistance and flexural strength of carbon samples.

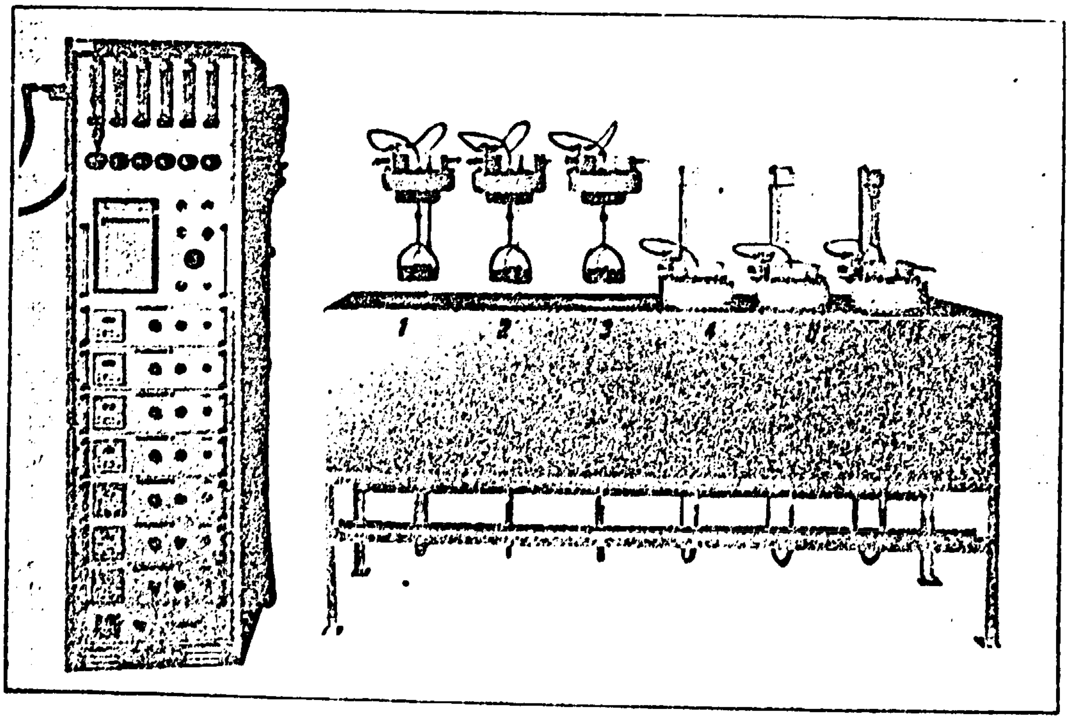


Fig. 14

F 6 Automat

Apparatus for the determination of the CO_2 burning behaviour of anodes.

Correlation between the Physical Properties of Pilot and Production Anodes

Selection of Raw Material

Example - Introduction of Petroleum Pitch

In the early 70's throughout the aluminium industry, attempts were made to replace coal tar pitch by petroleum pitch (1, 4, 8, 15).

From 1971 to 1973, ALUSUISSE conducted various tests with petroleum pitch. The typical properties of the pitch then used are given in Fig. 7 (type 72).

The test anodes, as well as the production anodes produced by pressing, were, in term of specific electrical resistance and flexural strength, not comparable with the standard coal tar pitch anodes. Based on these results, the tests were stopped. The Company producing the petroleum pitch continued the development at laboratory scale. Influence of the various distillation conditions were studied: pressure, temperature, heat soaking time. The samples tested in our anode pilot plant proved that an increase in the viscosity of the binder, achievable through a longer heat soaking time, led to a far better quality of anode. Based on these results, 40 tons of such a binder were produced (type 77, see Fig. 7).

The full sized pressed anodes produced with this new binder had a specific electrical resistance (61 Ω mm^2/m) and flexural strength (103 kp/m^2) comparable with anodes made with coal tar pitch.

This new binder was released for production use. It appears from this example that without the help of the pilot plant it would not have been possible to reach safely and at a low cost such a result.

Testing of New Formulations

Example - Mixing various petrol cokes

More and more often raw materials with below standard physical and chemical properties have to be used to produce anodes (15, 16, 17, 18). In order to maintain the quality of the anodes, they must be mixed with complementary types of material (2, 21).

BINDER: PETROL-PITCH

PROPERTIES	TYPE 72	TYPE 77
SOFTENING POINT METTLER	116 °C	124 °C
VISCOSITY AT 160 °C	3000 cP	7500 cP
TOLUENE INSOLUBLE	21 %	26 %
COKING VALUE	51 %	54 %

FIG.7

Properties of Petrol Pitches

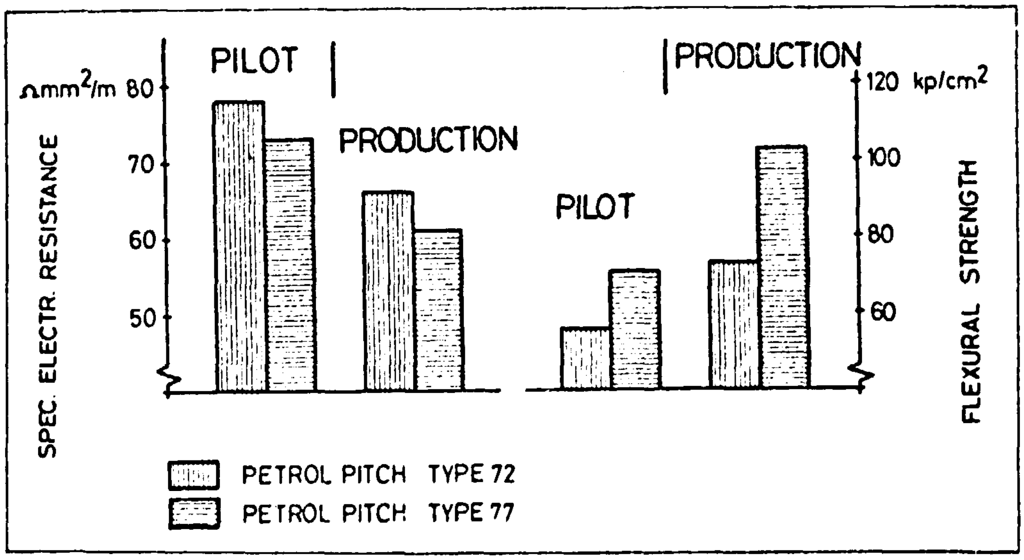


FIG.8

Physical Properties of prebaked Pilot- and Production Anodes prepared with Petrol pitch of different Types

One anode plant uses two types of petrol coke (A and B): Coke A is typically fitted for producing good quality anodes (Fig. 9), coke B does not meet the specifications and cannot be used alone. Both cokes had been mixed for years according to Recipe M.

To optimize the recipe, test anodes were produced in the pilot plant, combinations of cokes A and B in various granulometric fractions were tested. The best anode properties were obtained when coke A was used as dust and coke B in the larger fractions (Recipe P., Fig. 10).

Along with improvements of the electrical resistivity and the flexural strength, this new formulation led to a significant reduction of the carboxyreactivity.

These pilot plant results were confirmed in practice; a reduction of 10 g C/kg Al was noted in the pot rooms when anodes produced according to Recipe P were introduced.

Development of Process Standard Practices

Example - Final Baking Temperature

It is well known that anodes made of raw materials, coming from different sources, fabricated under the same conditions, do not have the same final properties. However, an increase of the final baking temperature can be used to accommodate some of those differences (1-5, 8, 9, 12-14, 19, 21, 22). An increase of the final baking temperature is nevertheless feasible only within certain economic limits set by:

- gas consumption
- cycle time
- quality of the refractory bricks.

In order to determine the baking temperatures for various materials with the goal of producing anodes which will have the same net anode consumption in the pot room, tests were conducted in the pilot plant and on the production lines.

Two different petrol cokes and one pitch coke were mixed with coal tar pitch under the same conditions. The green anodes made from these various materials were also baked under identical conditions. Fig. 11 shows the respective physical properties of the various cokes and the properties of the anodes obtained after baking.

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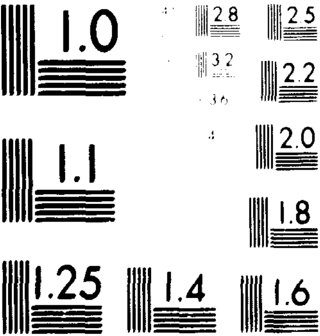

1.0
2.8
2.5
3.2
2.2
3.6
2.0
1.1
1.8
1.25
1.4
1.6

PROPERTIES	UNIT	PETROLCOKE	
		TYPE A	TYPE B
REACTIVITY LOSS	%	10 – 20	28
GRINDABILITY	%	80 – 86	75
BULK VOLUME 1 - 2mm	ml/100g	125 – 135	150

FIG 9

Physical Properties of Petrol Cokes

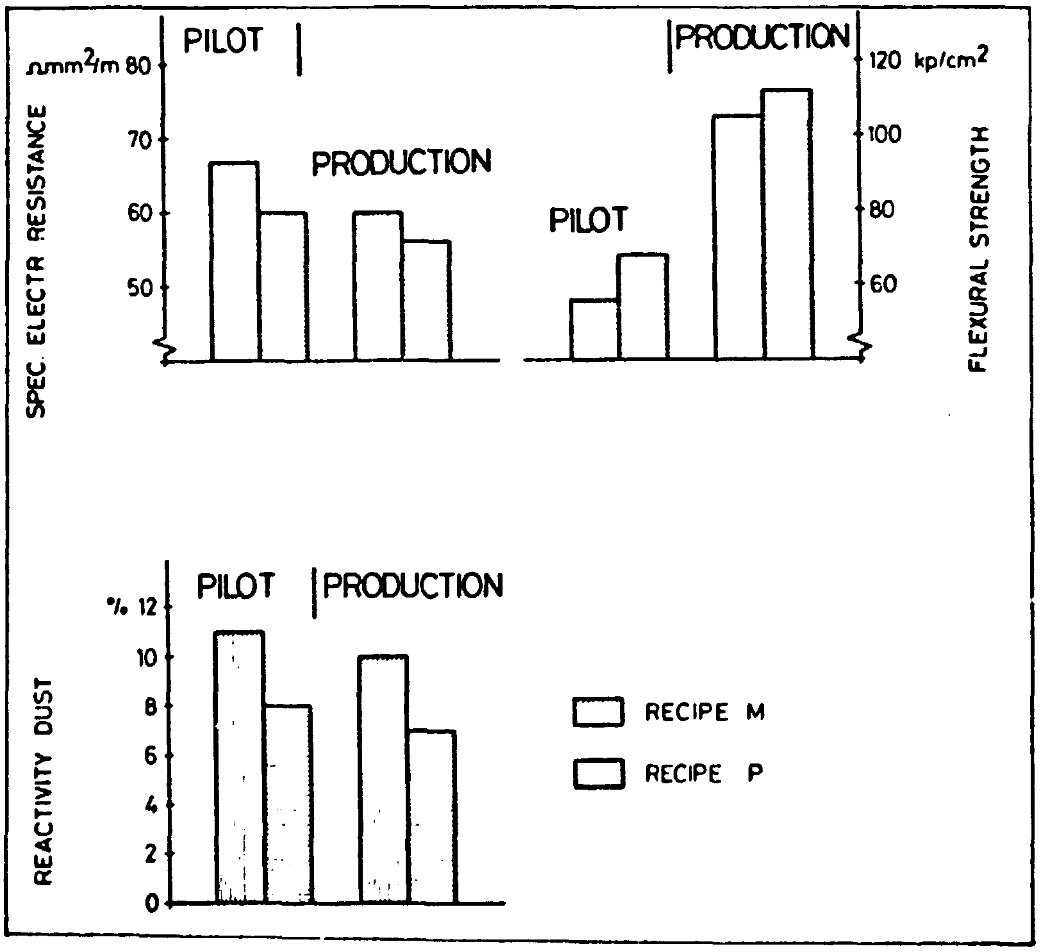


FIG. 10

Physical Properties of prebaked Pilot- and Production-Anodes containing blended Cokes in different size fractions.

The search for the optimal baking temperature for these various formulations on the production line would have been time consuming and costly. The balance of the experiments was carried out in the pilot plant.

Fig. 12 summarizes the results obtained with the three cokes in form of the relationship between the results of the carboxyreactivity test and the baking temperatures. To obtain 8 % dust after the carboxyreactivity test, the following respective temperatures have to be reached.

Petrol coke 1 - 1025°C
Petrol coke 2 - 1120°C
Pitch coke - 1165°C

The pilot plant work is beyond doubt very useful in such studies where process parameters have to be correlated with anode properties.

Conclusion

At the present stage of knowledge, the complexity of the problems involved in making prebaked anodes is such that experimental work remains mandatory. Furthermore, when these problems are rendered even more difficult by the necessity to use non-consistent raw materials, technical solutions can be found in operating a true pilot plant (Fig. 15).

The examples described above have demonstrated that the results of the pilot plant work could be introduced without restriction in the production lines and that a large spectrum of problems ranging from the influence of raw materials on anode quality to the design of process standard practices could be approached and solved in the pilot plant.

PROPERTIES OF COKES		PETROLCOKE 1		PETROLCOKE 2		PITCHCOKE	
REACTIVITY LOSS	[%]	14		22		20	
GRINDABILITY	[%]	74		81		84	
BULK VOLUME 1-2mm	[ml/100g]	155		148		135	
PROPERTIES OF ANODES		PILOT	PROD	PILOT	PROD	PILOT	PROD
APPARENT DENSITY	[g/cm³]	1.46	1.51	1.48	1.52	1.53	1.55
SPEC ELECTR RESISTANCE	[Ω mm²/m]	60	57	57	55	68	65
FLEXURAL STRENGTH	[kp/cm²]	75	86	89	95	77	88
REACTIVITY REST	[%]	81	79	70	69	75	72
REACTIVITY DUST	[%]	7	8	11	12	10	12

FIG 11

Physical Properties of Pilot- and Production Anodes Prepared with Cokes of Different Origin

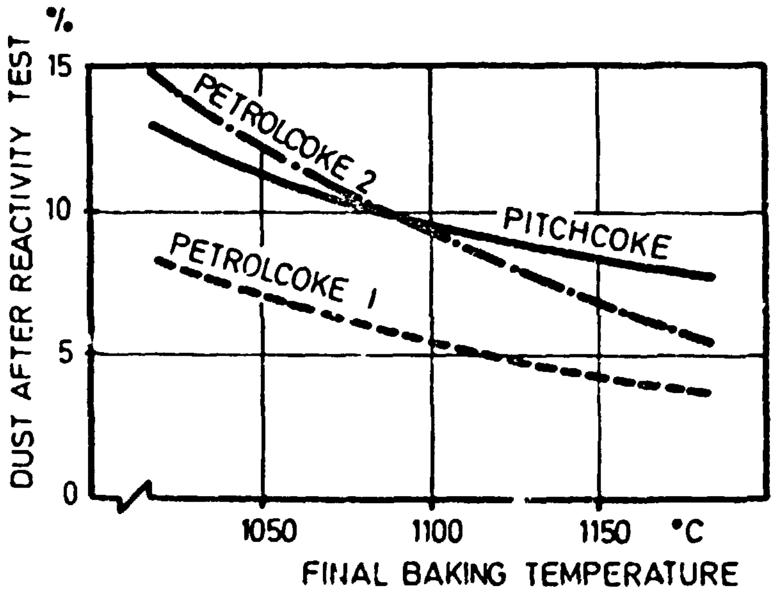
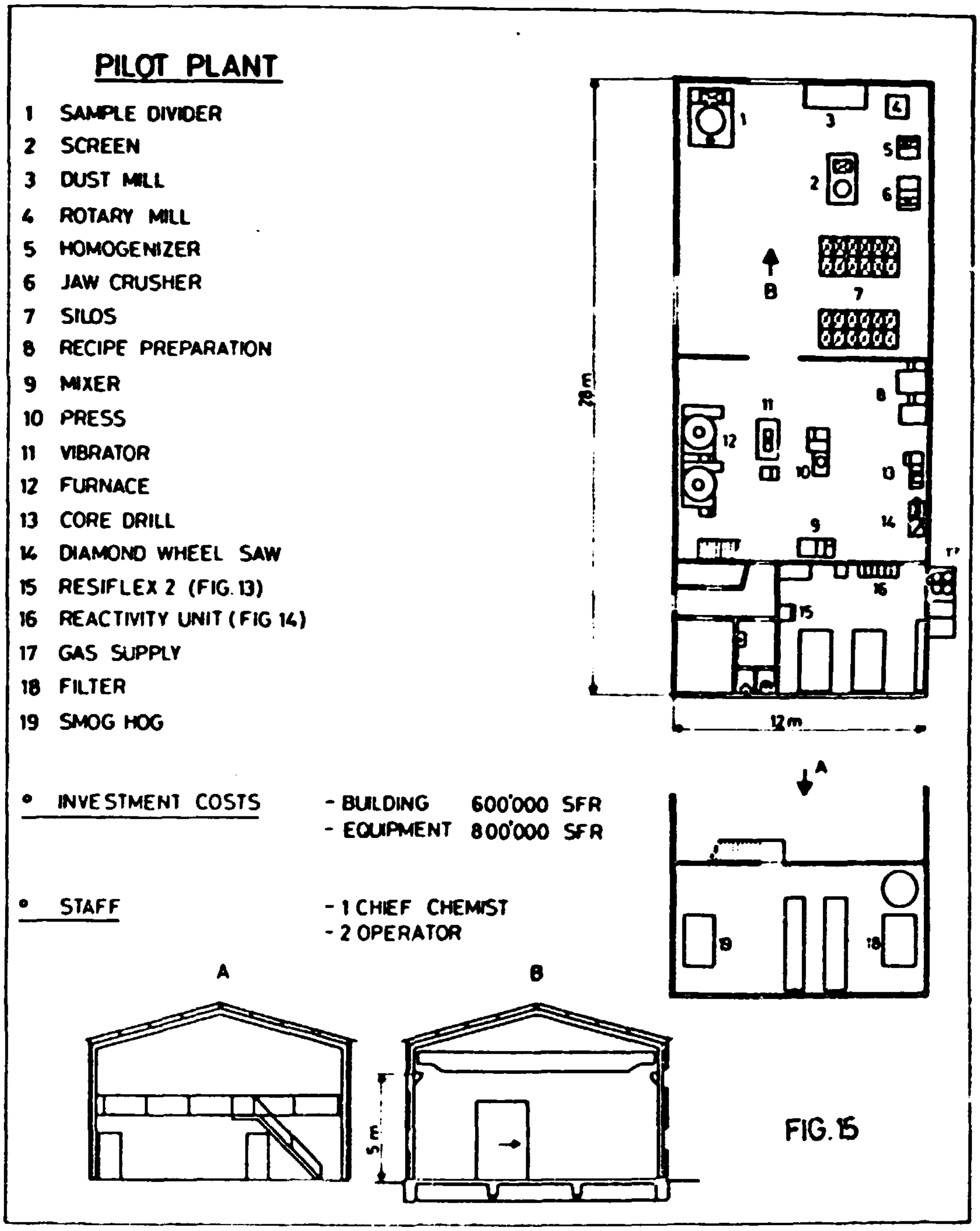


FIG. 12


PILOT PLANT

1 SAMPLE DIVIDER
2 SCREEN
3 DUST MILL
4 ROTARY MILL
5 HOMOGENIZER
6 JAW CRUSHER
7 SILOS
8 RECIPE PREPARATION
9 MIXER
10 PRESS
11 VIBRATOR
12 FURNACE
13 CORE DRILL
14 DIAMOND WHEEL SAW
15 RESIFLEX 2 (FIG. 13)
16 REACTIVITY UNIT (FIG 14)
17 GAS SUPPLY
18 FILTER
19 SMOG HOG

- INVESTMENT COSTS
  - BUILDING 600'000 SFR
  - EQUIPMENT 800'000 SFR

- STAFF
  - 1 CHIEF CHEMIST
  - 2 OPERATOR

FIG. 15

Lay-out of a Pilot Electrode Plant

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