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T I T L E : EURopean ANDalusite purified by original processes and industrial testing as high quality REFractory

(EURANDREF)

PROJECT
COORDINATOR: DAMREC - Division de Glome

PARTNERS : Krupp - Hoesch Stahl AG - Refractory Laboratory

University Catholique de Louvain la Neuve
Département des Sciences des Matériaux et des Precedes
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EURopean ANDalusite purified by original processes and industrial testing as high quality Refractory (EURANDREF)

Authors : Jean Philippe Beuvelet (1), Dr Andreas Buhr (2), Dr André Van Lierde

ABSTRACT '

Andalusite ($Al_2O_3.SiO_2$) is an industrial miners. introduced in the european industry as a refractory material in the 70's. The coarse raw material (> 0.4 mm), now on the 'market, has more than 0.9 % Fe_2O_3 which is the main impurity.' The three main partners of this project have carried out a complete work programme :

- purification of andalusite, using original processes (acid leaching, calcination + magnetic separation, . ..). to produce, at the labx-story and then at the pilot plant, concentrates with the lowest iron content (<: 0,6 % Fe_2O_3).
- production of low iron andalusite refractory materials (bricks and castables) with the help of european refractory producers.
- testing at the laboratory, and then in industrial conditions of a steel plant, the new low iron andalusite refractories.

The new refractories developed have good thermomecanical data, particularly resistance to CO gas. Applications for continuous steel casting (tundishes), safety lining of steel ladles, special parts in blast furnaces and also in ceramic and glasss industry, could be achieved, using these new european low iron andalusite refractories"

(1) - DAMREC - Division Ouest - Guerphalès - F 22110 GLOMEL FRANCE

(2) - KRUPP-HOESCH Stahl AG - Refractory Materials Laboratory -20 GMT - STP G 44120 DORTMUND GERMANY

(3) - UNIVERSITE CATHOLIQUE DE LOUVAIN-LA-NEUVE - Unite des Precedes Place Sainte-Barbe, 2- B 1348 LOUVAIN-LA-NEUVE BELGIUM

INTRODUCTION

Andalusite is a natural alumino-silicate which belongs to the sillimanite minerals ($Al_2O_3.SiO_2$). These minerals convert to mullite ($3\,Al_2O_3.2SiO_2$) when firing. Andalusite transforms to mullite at 1380 'C with low expansion(5%). Andalusite is mainly used in the steel industry as it imparts good refractoriness, loading capacity at high temperature, resistance to thermal shock, high creep resistance and resistance to chemical attack and abrasion.

Andalusite world-wide production is about 300030-350000 tpa and is only industrially mined in Republic of South Africa and in France. The main impurity in the raw material is iron, which exists in the concentrates in the range 0.8 - 1.1 % Fe_2O_3. The european andalusite, is more and more in competition with low cost south-african andalusite and chinese bauxite. Therefore there are several opportunities to produce a better raw material :

- an iron content, lower than 0.6 % Fe_2O_3, must led to a material with better thermomecanical data up to 1 700°C,
- an iron content lower than 0.6 % Fe_2O_3 gives to the material a typical white colour after firing. On the contrary the brown dark spots, due to iron bearing minerals, should decrease strength of the refractory to CO gas.

Studies achieved a few years ago, carried to a new original flow-sheet, using flotation, to process fine particles of european andalusite (O. 05-0..35 mm). Nowadays, this process is used to produce the purest andalusite material available on the world-wide market : Kerphalite KF ($Al_2O_3 > 60\%$ and $Fe_2O_3 < 0.5\%$).

The main objectives of the project are as follows :

1. to find original processes, to produce a new coarse size (0.3 - 1.6 mm) andalusite material with the lowest iron content ($\leq 0.6\%$ Fe_2O_3) which is the main impurity,
2. to produce new refractory materials, bricks and castables, using low iron andalusite,
3. to test, using industrial conditions in a steel pant, these new refractories in comparison with standard andalusite refractories and competitive materials, '
4. evaluation concerning the use of purified andalusite in different industrial furnaces.

TECHNICAL DESCRIPTION

Purification test work

Two representative samples of thousand tons of european andalusite raw materials were selected (see Figure 1). Chemical and mineralogical studies have shown that iron impurity is beared by biotite (micas) and pyrite (FeS2), while the iron content of andalusite is about 0.4 % Fe2O3. One must notice that, only iron coming from biotite or pyrite produces dark spots on andalusite bricks or castables after firing.

University Catholique de Louvain (UCL) and DAMREC have developed, at the laboratory, new processes to produce low iron content andalusite concentrates :

- Epuration by acid leaching : The work carried out by UCL has shown that it is possible to reach the target of iron epuration, using a new process by acid leaching (H2S04 + HNO3 or HCl + HNO3). After leaching by impregnation or percolation, the purified concentrates assay less than 0.55 % Fe2O3 with a very good yield.
- Epuration by calcination followed by High Gradient Magnetic Separation,: The aim is to transform non magnetic pyrite (FeS2) into paramagnetic pyrrhotite (FeS) by roasting. Then pyrrhotite, locked particles of pyrrhotite-andalusite, and locked particles of biotite-andalusite, are removed by high gradient magnetic separation (HGMS). After roasting, one step of magnetic separation, using permanent "magnet roll, is sufficient to decrease iron content in the concentrates until 0.55 % Fe2O3. Nevertheless the yield of purified concentrate, is lower compared to acid leaching.
- Epuration using other processes :
  - ✓ Gravity separation (spirals, cone, heavy media separation, . ..) has been tested to remove free particles of pyrite. It is possible, using these techniques, to decrease iron content, but it is not possible to reach 0.6 % Fe203, as locked particles of pyrite-andalusite and biotite-andalusite still remain in the concentrate.
  - ✓ Bio-leaching using acidic water from the andalusite quarry has been successfully tested to remove pyrite. Adding one step of magnetic separation allows' to reach 0.65 % Fe2O3 in the concentrate, with a good yield. Nevertheless the duration of bio-leaching is still very long at 20°C.

Except gravity separation, none of the processes tested is industrially used at present to purify andalusite. In order to create new refractories, samples of purified andalusite were produced at the Laboratory (UCL & DAMREC). Then, several hundred tons of purified andalusite (Kerphalite KF -0.6 % Fe2O3 -0.3- 1.6 mm) were produced at the pilot plant with a process using calcination and HGMS (see Figure 2).

Production of new andalusite refractories

Four european refractorists were selected by the steel producer KRUPP-HOESCH to create purified andalusite refractories. As they need a complete size distribution to produce bricks and unshaped refractories, the finer KF materials were delivered by DAMREC. These finer KF were produced using the flotation process, which was developed during a previous EC contract. The refractorists have given some refractory samples to test in KRUPP-HOESCH laboratory. Then several hundred tons of refractories, bricks and castables, were produced and delivered to the steel plant.

Refractory testing

- Torpedo cars lining

Torpedo cars are used to transport pig iron from the blast furnace to the steel plant. The capacity of each ladle is 200 tons of pig iron which has to be kept between 1 45-O and 1 500 "C during several hours. Refractory bauxite or andalusite bricks are usually used (50 tons per torpedo car). The lining life correlates to -125 000 tons of pig iron (-10 months). The table I below, gives the chemical content of competitive bricks.

%	Bauxite	Standard Andalusite	EURANDREF KF Andalusite
SiO2	11,70	37,00	36,30
Al2O3	81,80	60,60	61,10
Ti02	3,40 ",	0,27	0,17
Fe203	1,30	0,95	0,63
CaO	0 > 3 0	0,10	0,07
MgO	0,50	0,15	0,13
Na20	0,10'	0,08	0,06
K20	0,40	0,34	0,11
Loss on ignition	0,10	0,1(	0,09
T o t a l	99,60	99,59	98,66
Bulk density (g/cm')	2,70	2,59	2,60

Table I : Chemical analysis of high quality fired Bauxite and Andalusite bricks

The CO-resistance is very important for blast furnace lining, torpedo car safety lining and in many other furnaces. A KF andalusite brick was tested, at the laboratory, in comparison with standard andalusite bricks for torpedo cars. The results given in Table II show that standard andalusite bricks have a good CO-resistance when firing temperature is high. However, low iron andalusite bricks (KF) have a better CO-resistance with a lower firing temperature. This fact could be very important for using such bricks for special parts in blast furnaces.

	Standard andalusite bricks				EURANDREF KF andalusite brick
	1	2	3		
Fe2O3 %	1,06	0,99	0,97		
Firing temperature "C	1 480	1 280	1 320	1 300	1 220
CO - Resistance	Good	little resistance			Very good

Table 11: Comparison of andalusite bricks versus CO-resistance

Industrial tests were carried out with three torpedo cars lined with KF bricks. Unfortunately, there was no benefit for KRUPP-HOESCH to use low iron andalusite as refractory in contact with pig iron, Nevertheless it could be of interest to test this material for blast furnaces and also as insulating material.

- Steel ladles lining

Steel ladles are crucibles used for transportation, treatment and casting liquid steel. Each KRUPP-HOESCH ladle contains 200 tons of steel at 1630 - 1730 'C. Previous studies have shown that bauxitic castables, lined using a casting method, present several advantages. KF andalusite based castables were produced and tested at the laboratory. These new refractories show good thermomecanical datas at the laboratory. They were tested in industrial conditions as wear lining and safety lining (see Figure 3). Results for wear lining were not interesting, as the composition of the slag in the ladles has changed due to metalurgicall constraints (see Table III).

Results for safety lining of steel ladles are promising. The lining life of safety lining is twice higher when KF andalusite castable is used, in comparison with bauxitic castables, when the double wall lining technique can be used in the steel plant.

Assay %	1993	1995
Cao	30	40
Al2O3	50	40 - 50
SiO2		5
Fe	4	4
Mno ,	1 - 2	1 - 2
MgO	7	5
Total		95 - 100
CaO / Al2O3	0,60	0.9 - 1.0

Table 111: Evolution of the slag in the KRUPP-HOESCH steel ladles

- Tundishes lining

Tundishes are special crucibles used for the continuous steel casting. KRUPP-HOESCH tundishes have a capacity of 40 tons steel at 1500-1550 'C. The permanent lining is andalusite base castable which has a lining life of 12 months. The wear lining, magnesite/olivine gunning material, is removed every four tasted steel ladles under stresses, and the tundish is cooling down from 1 500°C to less than 100"C at the time of relining the wear. Consequently, the tundi sh permanent lining must have a high thermomechanical stability and a good thermal shock resistance. Andalusite base castables are the best refractories for tundish permanent lining as shown in table IV.

Castable	Andalusite	Bauxite	Corundum
Number of castings	730 - 1 440	350 - 420	420

Table IV : Lining life of permanent lining

A new castable was developed using low iron andalusite (KF) and bauxite addition for grain sizes coarser than 2 mm. In comparison with standard andalusite castable, the new material has a lower iron content. The creep resistance at 1 500 °C is improved and the thermal shock resistance is excellent.

Industrial tests in the steel plant have demonstrated that it could be interesting to use the new low iron andalusite castable in the bottom of tundishes to reduce repairing efforts during lining life.

RESULTS AND CONCLUSIONS

Up to this project, there was no real research undertaken by producer and user of andalusite together, concerning low iron coarse gra n andalusite. Several real benefits were achieved by all partners :

- Several processes were tested at the laboratory in order to purify coarse grain european andalusite. Both of them give very good technical results.
- One purification process (Roasting + HGMS) was tested in a pilot plant. The results were as good as those achieved at the aboratory, dealing with iron content and yield.
- Several hundred tons of new coarse grain andalusite were produced at the pilot plant. Four european refractorists have produced several hundred tons of new low iron andalusite refractories (bricks and castables).
- All the new andalusite refractories produced, give good technical results at the laboratory. Then several hundred tons of new andalusite castables and bricks were tested in industrial conditions of an europea n steel plant.
- Technical and economical results do not seem interesting for steel ladles (when CaO is high in the slag) and torpedo cars. But lining the bottom of some tundishes with low iron andalusite castable could present interest.
- The new low iron andalusite refractory presents a very good resistance to CO attack. This could be interesting for special parts of blast furnace.
- Other refractory users (ceramic industry, glass industry,...) could be interested by these new low iron andalusite refractories.

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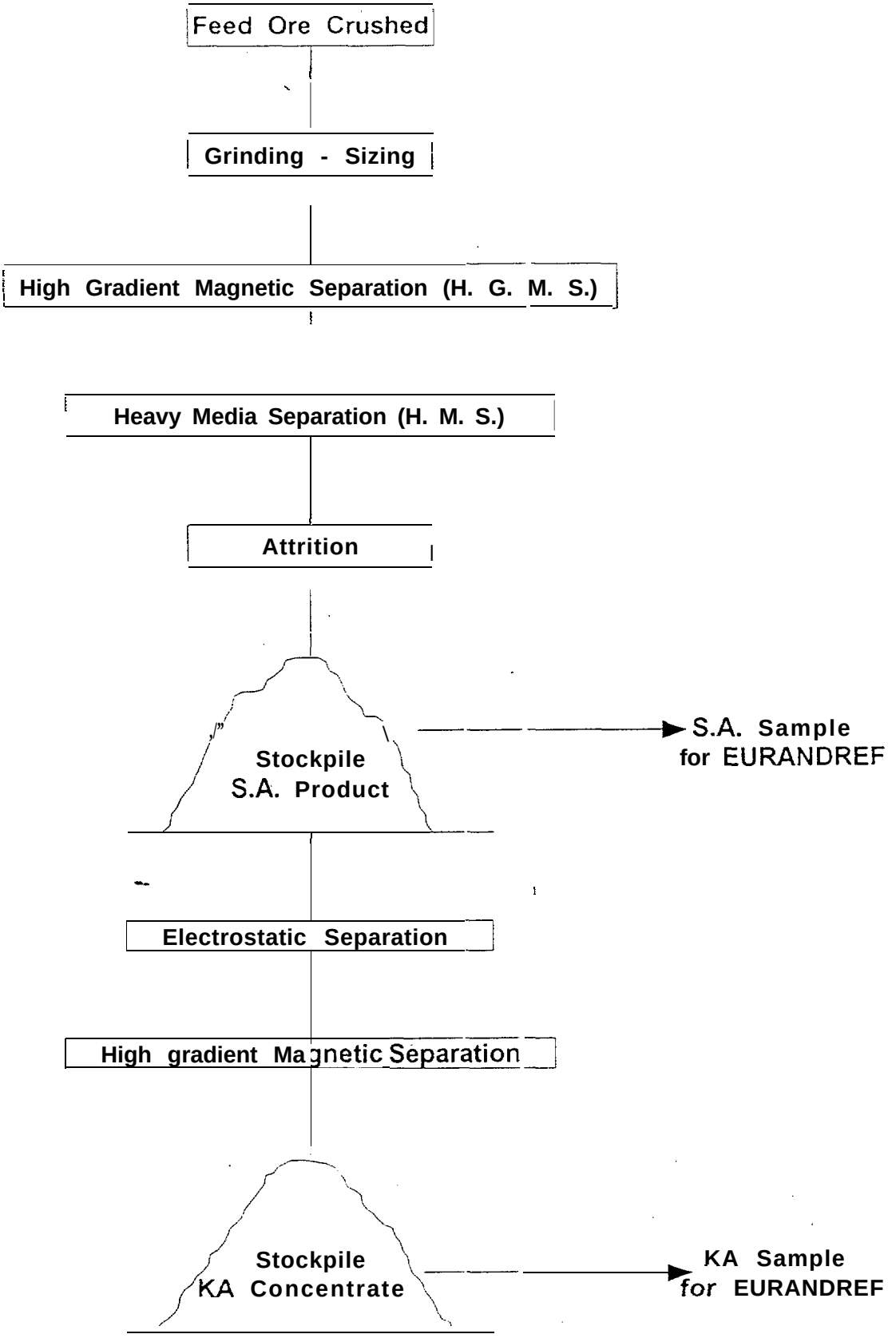
All partners miss Dr Manfred Koltermann, who died on October lst, 1996. He was in charge of the Refractory Laboratory at KRUPP -H OESCH. Everybody has in mind his great experience of refractory and efforts to achieve this project. All the partners will regret his kindness and professionalism.

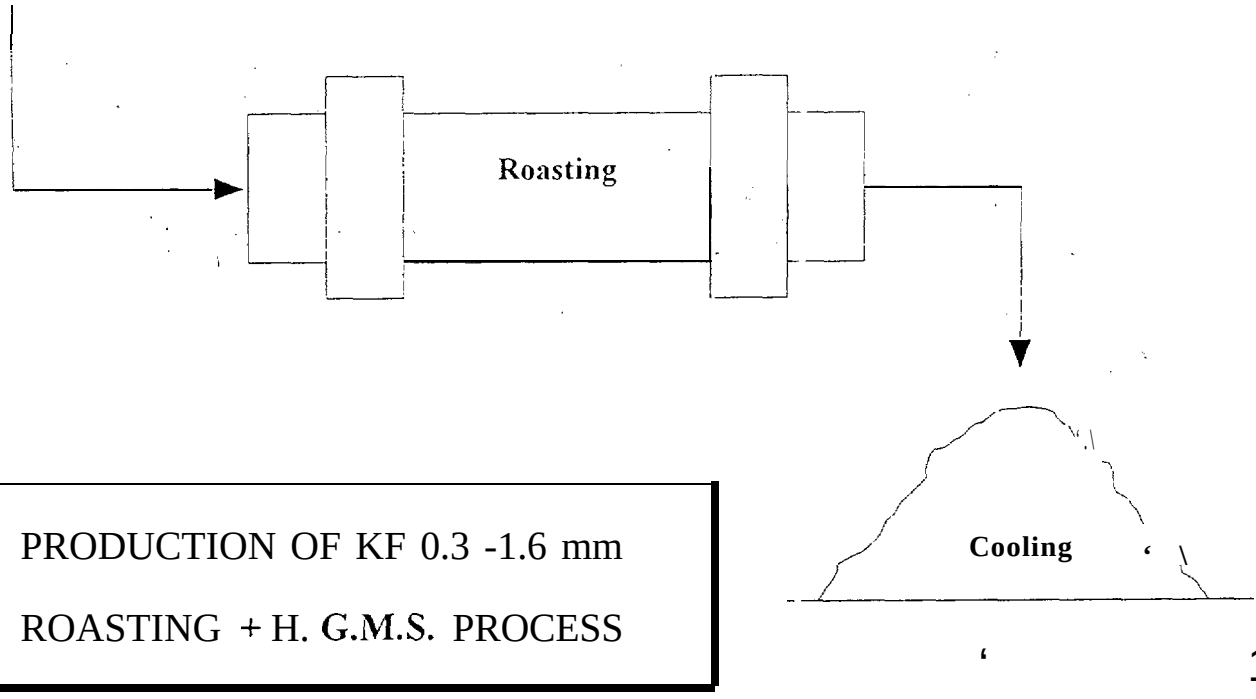
Summarised beneficiation process in DAMREC plant (Glomel)



JP8

17mm7

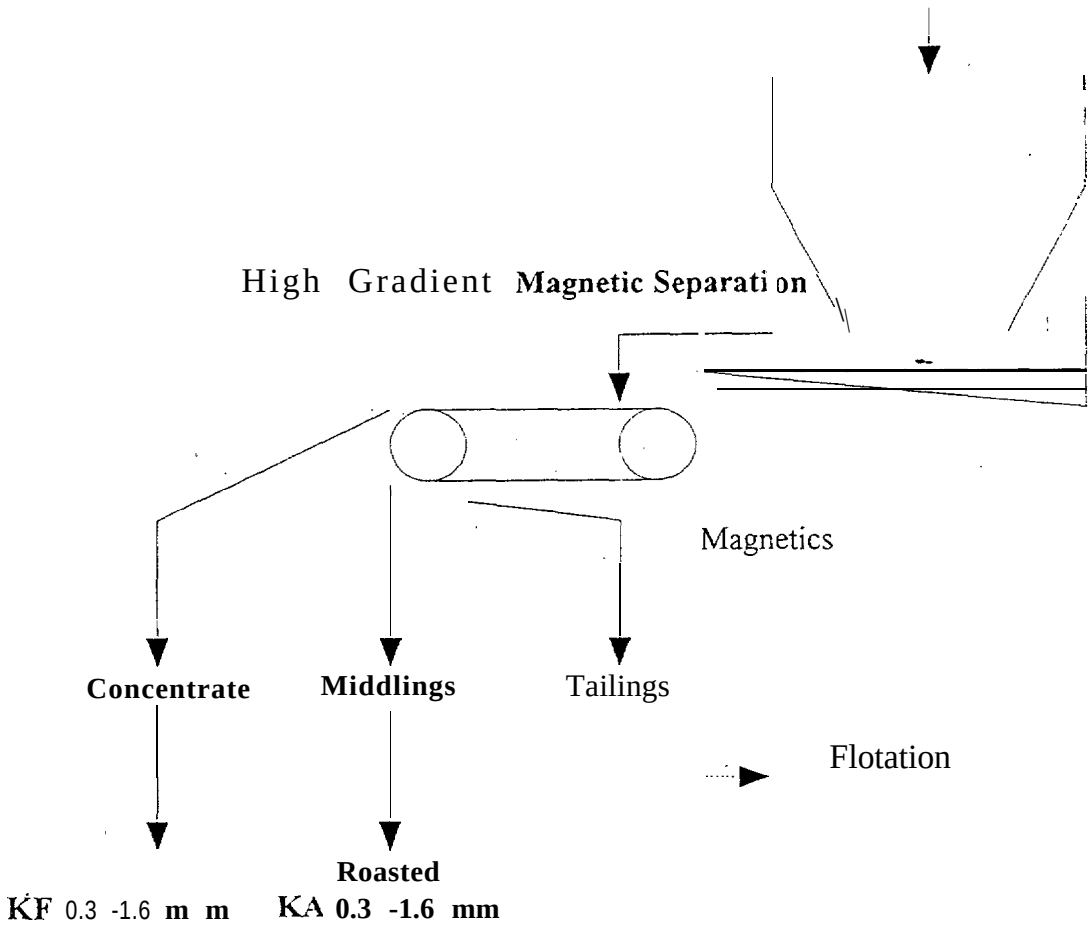
KA 0.3 -1.6 m m



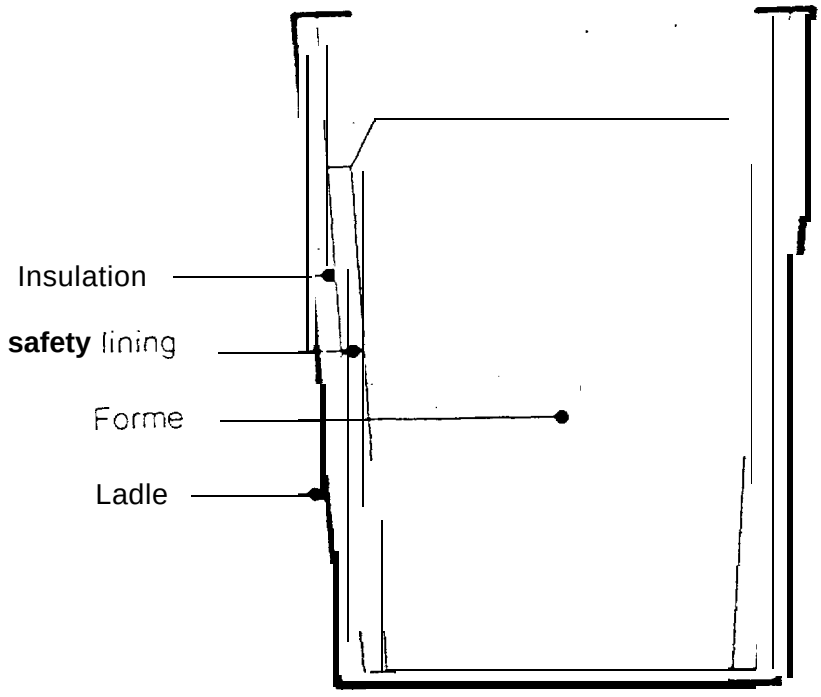
PRODUCTION OF KF 0.3 -1.6 mm

ROASTING + H. G.M.S. PROCESS

1

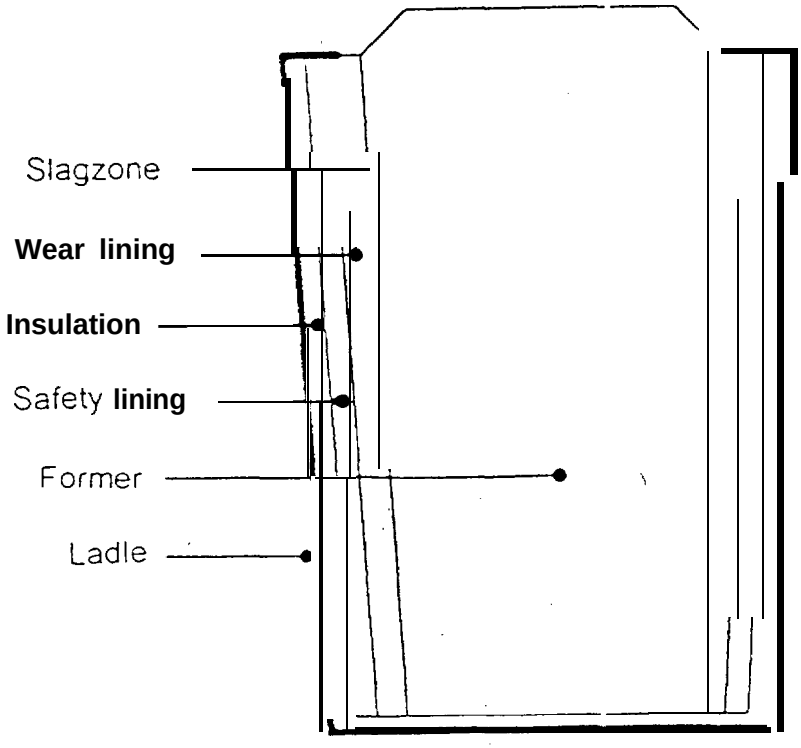


KA 0.5-0.35 m m



safety **lining:**
Bauxite - Or
Andalusite -
castable

Casting **of safety lining with former 1**



wear **lining:**
Bauxite - or Spine{ -
castable

Casting of wear lining with former 2