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ELECTRODE TECHNOLOGY for ALUMINUM PRODUCTION

Anode Raw Materials and Green Carbon

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PROPERTY PROFILE OF LAB-SCALE ANODES PRODUCED WITH 180 °C METTLER COAL TAR PITCH

Winfried Boenigk, Claudia Boltersdorf, Falk Lindner, Jens Stiegert
RÜTGERS Basic Aromatics GmbH; Kekuléstraße 30, 44579 Castrop-Rauxel, Germany

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Abstract

The PAH-induced toxicity of coal tar pitch decreases with increasing softening temperature. The use of high- melting pitches is however restricted due to operational challenges. One critical limitation is high-temperature mixing. Temperatures up to 300 °C were now realized using a newly developed EIRICH mixer. A 180°C Mettler binder pitch resulted in lab-scale anodes having a higher baked density (+0.04 g/cm³). Electric resistivity and air permeability are reduced whereas compressive strength and Young's modulus are increased. The significantly lower baking loss allows a faster carbonisation process in the low temperature range, potentially increasing the throughput of baking furnaces.

Introduction

Aluminum is a versatile engineering material and can contribute significantly to reduce energy consumption when used for car production. An unwelcomed by-product of aluminum production is CO_2 released during electrolysis. The carbon footprint of aluminum production needs to be improved e.g. by optimizing carbon anode performance Coal tar pitch (CTP) will remain the predominant anode binder for the foreseeable future despite its content of carcinogenic polycyclic aromatic hydrocarbons (PAHs). The potential for CTP to contribute to an even brighter future of aluminum production is not yet exhausted. Reduction of CTP toxicity and an increase in anode density are main improvement targets in aluminum production. The best established method to measure pitch toxicity has been introduced by Alcan in cooperation with CANTOX [1,2]. One approach to lower pitch toxicity applicable to dry-paste Soederberg plants is blending CTP with petroleum pitch [3]. Obviously the removal of low molecular weight PAHs is more efficient than dilution [4]. One challenge for plant-scale use is the increase of CTP viscosity with decreasing toxicity.

For pitch qualification RÜTGERS operates an R&D Carbon bench scale plant [5]. It consists of an oil-heated mixer and a floating- mould press limited to 250 °C: sufficient for state of the art pitches but limiting investigations going beyond. In 1992 first attempts were made to produce anodes with high-softening pitch (170 °C Mettler) [6] expecting denser anodes and correspondingly lower specific electrical resistivity. A higher amperage would increase cell efficiency. EIRICH has recently introduced a new mixing system capable to operate up to 300 °C by introducing the inductive heating concept. This new EIRICH mixer allows for evaluation of pitches which soften up to 200 °C. Lab anodes were produced and analysed using a commercial Bx95 CTP and a 180 °C Mettler CTP at comparable viscosities.

Raw materials

For the lab scale anode production a mixture of two coke fractions is used (S = 2,26 %, Na = 143 ppm, Ca = 12 ppm). The sieve analysis of the dry recipe is shown in Fig.1.

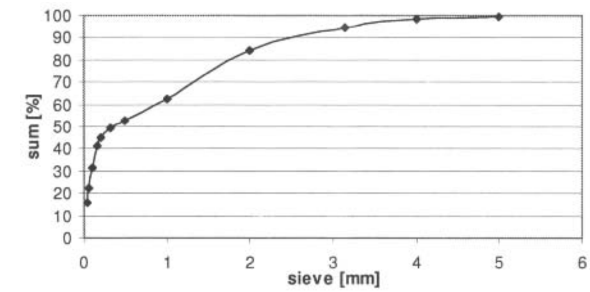

Figure 1: Coke particle size distribution

The characteristics of the trial pitches are shown in Table 1.
As expected the high softening point of HM 180M pitch results in a carbon yield of 76% instead of 58% of the standard CTP Bx95. The CANTOX-toxicity of HM180M pitch is reduced by 87% compared to CTP Bx95.

Table 1: Analytical properties of the investigated pitches

			Bx95		HM 180M	
Softening point Mettler	DIN 51920	[°C]	118		183	
Coking value (Alcan)	DIN 51905	[%]	57,9		76,4	
Toluene Insoluble	DIN 51906	[%]	29,9		43,1	
Quinoline Insoluble	DIN 51921	[%]	7,9		13,3	
Distillate 020 - 230°C	GC	[%]	0,01		0,04	
Distillate 230 - 270°C	GC	[%]	0,09		0,00	
Distillate 270 - 360°C	GC	[%]	1,10		0,01	
Distillate 360 - 440°C	GC	[%]	4,81		0,13	
Distillate 440 - 500°C	GC	[%]	12,53		1,88	
Distillate >500°C	GC	[%]	14,06		13,37	
Sum of Distillates	GC	**[%]**	**32,60**		**15,44**	
GC-analysis		RPF(Canto:	PAH[ppm]	BaP-equiv	PAH[ppm]	BaP-equiv
Naphthalene		0,000	24	0	0	0
Acenaphthylene		0,000	0	0	0	0
Acenaphthene		0,000	488	0	0	0
Fluorene		0,000	116	0	0	0
Phenanthrene		0,000	3276	0	0	0
Anthracene		0,000	658	0	0	0
Fluoranthene		0,034	10018	341	81	3
Pyrene		0,000	8666	0	89	0
Benzo[a]anthracene		0,033	7748	256	235	8
Chrysene		0,260	8253	2146	282	73
Benzo[e]pyrene		0,050	8345	417	1111	56
Benzo[b]fluoranthene		0,100	12090	1209	1198	120
Benzo[k]fluoranthene		0,010	6045	60	599	6
Benzo[a]pyrene		1,000	10307	10307	1608	1608
Dibenzo[a,h]anthracene		1,400	2141	2997	721	1009
Benzo[ghi]perylene		1,000	8097	8097	462	462
Indeno[1,2,3-cd]pyrene		0,100	7702	770	3490	349
Total			**93974**	**26600**	**9876**	**3694**
Average toxicity index				**1**		**0,13**

EIRICH inductively heated mixer [7]

To realize high heat flows into the mixture / material to be heated high temperature gradients between the product and the wall are necessary. In wall heated, batch wise operated heating systems the speed determining factor is usually given by the energy supply through the external heating system, which determines if and by how much the wall temperature drops after the addition of cold material and especially how fast the temperature rises again to the set point. When using a liquid heat transfer medium to heat the outer wall of a mixer the limitation is mainly given by the heat transfer between heating medium and chamber wall. The heat transfer will improve when using turbulent flow but is usually limited by the double-shell geometry and high pressure drops. A particularly efficient method in terms of heat transfer, uniformity of heat distribution on the heating surface and regulation of the heating power provides the newly developed and patent pending induction heating system of the rotating mixing chamber in an Eirich mixer.

Due to the high energy output between the inductor and the rotating mixing chamber the user can realize extremely fast heating curves, high wall temperatures, short drying times as well as high product temperatures up to 250-280 °C.

The inductively heated mixer consists of a rotating mixing chamber moving the process material into the zone of the eccentric quick-running mixing tool. The mixing chamber as well as the mixing tool are equipped with their own drives enabling the adaptation of the speeds to the individual application and to the process material. The combination of the mixing chamber and the mixing tool rotation as well as the inclined arrangement of the mixing chamber causes the generation of an intensive three-dimensional fluid bed-like material flow in the mixer interior in connection with a stationary material deflector at the chamber wall. The constructive design of the mixing tool with knife-type mixing blades, high peripheral speeds as well as the opposed rotating direction to the mixing chamber, enable an intensive circulation and the surface of the process material is "ripped" open. In the granulation phase, the opposing movement results in a mechanically generated fluidized bed which presents the condition for maximum heat and mass transfer. The stationary material deflector also reliably avoids cakings on the wall and the bottom and facilitates the discharge of the material through the discharge flap in the centre of the rotating mixing chamber bottom.

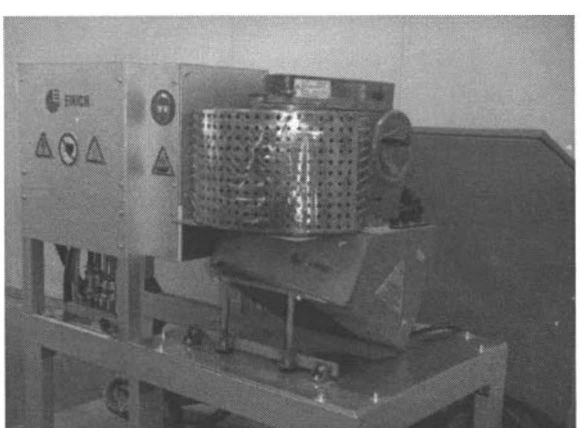

Figure 2: Mixer with inductive heating

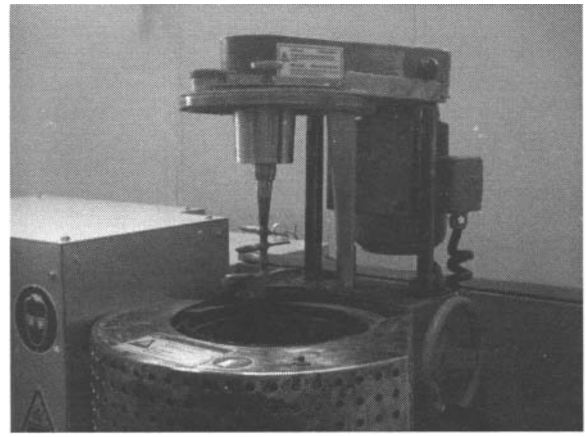

Figure 3: Opened lab scale EIRICH mixer with stirrer removed

Production parameters

The EIRICH intensive mixer used for the experiments has a volume of 5 L with a diameter of 235 mm. The mixing vessel (42 rpm) and the stirrer (900 rpm) rotate in the same direction. The mixing time is 9 min to reach 280 °C with a pre-heated coke and cold solid pitch for the high melting pitch and 4 min to reach 210 °C for the standard binder pitch. The pitch content in the batches was selected in the range from 14 to 18 w.-%. From each batch 13 anodes with a diameter of 50 mm and a height of 100 mm are prepared. Therefore nearly 350 g of the mixture are necessary. The anodes are pressed with 120 kN corresponding to 600 bar.

Results

After production of the anodes the following characteristic data were collected:

apparent green density, apparent carbonized density, baking loss, coking yield, volume expansion, compressive strength, Young's modulus, air permeability, specific electric resistance, CO_2-reactivity.

The anode properties are shown in Tables 2 and 3.

Using the high melting pitch an increase of 0.05 g/cm³ of the green density is possible for all examined pitch contents (Figure 4) which translates to a similar difference in density after baking (Figure 5).

Using the standard pitch leads to a density of 1.59 g/cm³ whereas the high melting pitch results in a significant increase in density of 1.63 g/cm³.

The baking loss of the anodes is less than 4 % for the high melting pitch while it is more than 5% for the standard pitch (Figure 6). In correlation to this the coking yield increases from 67 to more than 80% (Figure 7). This is a direct result of the higher coking value of the high melting pitch, HM 180 M.

The significantly lower baking loss of the anodes produced with the high melting pitch and the reduced volatiles of HM 180M (Table 1) very likely allow a faster carbonization program for anode preparation. This was tested subsequently and confirmed on lab scale.

The carbonization program sequences used are shown in Tables 4 and 5.

Table 2: Properties of bench scale anodes

		Eirich Mixer BX 95		Eirich Mixer HM 180	
	Pitch Content [%]	Normal Carbonization	Fast Carbonization	Normal Carbonization	Fast Carbonization
Apparent green density [g/cm³]	14	-	-	1.656 (0.014)	1.653 (0.018)
	15	1.644 (0.004)	-	1.686 (0.007)	1.679 (0.007)
	16	1.664 (0.003)	1.667 (0.004)	1.713 (0.004)	1.688 (0.019)
	17	1.672 (0.003)	-	1.726 (0.004)	1.721 (0.009)
	18	-	-	-	-
Apparent carbonized density [g/cm³]	14	-	-	1.624 (0.013)	1.624 (0.018)
	15	1.583 (0.004)	-	1.645 (0.004)	1.627 (0.003)
	16	1.591 (0.003)	1.589 (0.003)	1.637 (0.010)	1.63 (0.007)
	17	1.582 (0.004)	-	1.629 (0.009)	1.615 (0.012)
	18	-	-	-	-
Baking loss [%]	14	-	-	2.7 (0.1)	2.8 (0.1)
	15	4.9 (0.1)	-	2.9 (0.1)	3.0 (0.1)
	16	5.3 (0.1)	5.9 (0.1)	3 (0.1)	3.3 (0.1)
	17	5.9 (0.2)	-	3.1 (0.2)	3.5 (0.1)
	18	-	-	-	-
Coking yield [%]	14	-	-	81 (0)	80.1 (0)
	15	67.2 (0)	-	81 (0)	80.1 (0)
	16	66.7 (0)	63.2 (0)	81.1 (0)	79.6 (0)
	17	65.2 (0)	-	81.7 (0)	79.3 (0)
	18	-	-	-	-
Volume expansion [%]	14	-	-	−0.6 (0.1)	−1.0 (0.2)
	15	−1.2 (0.2)	-	−0.5 (0.3)	0.2 (0.3)
	16	−1 (0.2)	−1.3 (0.2)	0.6 (0.9)	0.4 (0.4)
	17	−0.6 (0.3)	-	1.7 (1.3)	2.8 (0.4)
	18	-	-	-	-
Compressive Strength [MPa]	14	-	-	51 (3)	44 (3)
	15	39 (2)	-	54 (0)	54 (0)
	16	40 (3)	35 (1)	55 (0)	54 (0)
	17	42 (2)	-	54 (0)	53 (0)
	18	-	-	-	-

Values in brackets represent standard deviations.

Table 3: Further anode properties

		Eirich Mixer BX 95		Eirich Mixer HM 180	
	Pitch Content [%]	Normal Carbonization	Fast Carbonization	Normal Carbonization	Fast Carbonization
Young's Modulus [GPa]	14	-	-	2.3 (0.4)	2.1 (0.4)
	15	2.2 (0.1)	-	2.8 (0.2)	2.9 (0.2)
	16	2.3 (0.2)	2.2 (175)	3.5 (0.2)	3.1 (0.3)
	17	3.4 (0.4)	-	3.4 (0.5)	3.3 (0.5)
	18	-	-	-	-
Air-Permeability [nPm]	14	-	-	0.4 (0.3)	0.3 (0.2)
	15	0.4 (0)	-	0.1 (0)	0.17 (0)
	16	0.5 (0.1)	0.4 (0)	0.2 (0)	0.5 (0.2)
	17	0.7 (0)	-	0.3 (0.1)	0.4 (0)
	18	-	-	-	-
Specific Electric Resistance [□□m]	14	-	-	62.2 (4.9)	63.4 (6.1)
	15	74.3 (7.6)	-	52.4 (1.9)	52.8 (2.7)
	16	60.9 (3.5)	61.2 (1.4)	46.9 (0.6)	49 (1.3)
	17	54.7 (0.5)	-	47.3 (4.3)	45.8 (0.8)
	18	-	-	-	-
CO_2-Reactivity residue [%]	14	-	-	82.0 (2.0)	84.8 (2.7)
	15	84.5 (1.1)	-	84.8 (1.8)	86.5 (2.6)
	16	85.2 (2)	82 (0.9)	84.4 (3.1)	87.2 (1.2)
	17	86.4 (1.1)	-	83.2 (2.7)	89.3 (0.8)
	18	-	-	-	-
CO_2-Reactivity dust [%]	14	-	-	7.9 (1.3)	6.4 (1.7)
	15	6.5 (0.7)	-	6.3 (1.0)	5.4 (1.7)
	16	6.0 (1.2)	8.1 (0.8)	6.8 (2.0)	4.7 (0.6)
	17	4.8 (0.5)	-	7.1 (1.8)	3.2 (0.4)
	18	-	-	-	-
CO_2-Reactivity loss [%]	14	-	-	10.1 (0.7)	8.8 (1.1)
	15	9.0 (0.4)	-	8.9 (0.8)	8.1 (1.0)
	16	8.8 (0.8)	9.9 (0.4)	8.8 (1.2)	8.1 (0.6)
	17	8.9 (0.6)	-	9.7 (1.0)	7.5 (0.4)
	18	-	-	-	-

Values in brackets represent standard deviations.

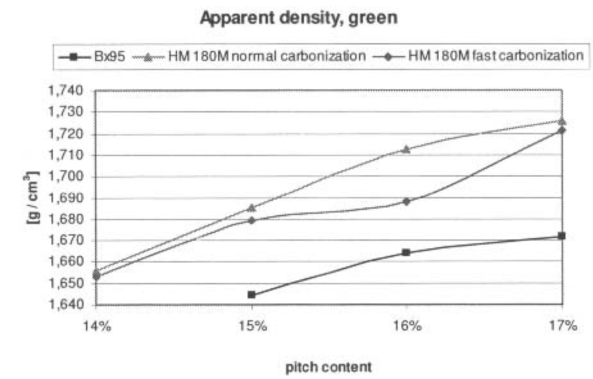

Figure 4: Apparent green density versus pitch content

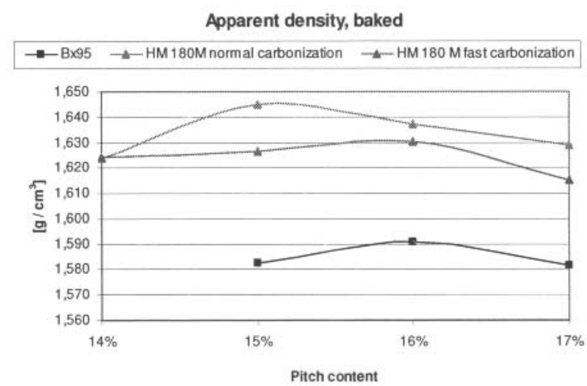

Figure 5: Apparent carbonized density versus pitch content

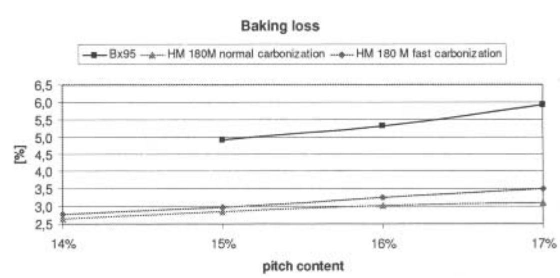

Figure 6: Baking loss versus pitch content

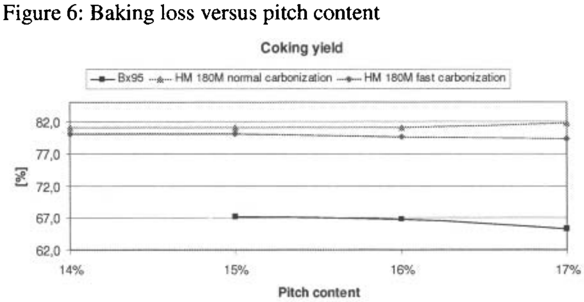

Figure 7: Coking yield versus pitch content

Table 4: Normal carbonization program

Temp. Beg	Temp. End	Gradient	Time
°C	°C	°C/h	h
20	600	50	11.6
600	1,100	100	5
1,100			5
	Total	Carbonization Time	21.6

Table 5: Fast carbonization program

Temp. Beg	Temp. End	Gradient	Time
°C	°C	°C / h	h
20	250	100	2.3
250	600	75	4.7
600	1,100	100	5
1,100			5
	Total	Carbonization Time	17

With the high melting pitch the carbonization time is reduced about 4.6 h (21%) because the temperature gradient was increased in the lower temperature range.
The faster carbonization program has only a small influence on the densities of the anodes. It might be possible to use faster heating programs for anode production. This could be an interesting aspect for anode producers because they can raise the throughput of the baking furnace.

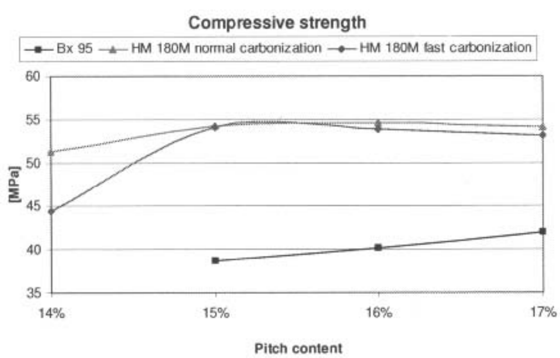

Figure 8: Compressive strength versus pitch content

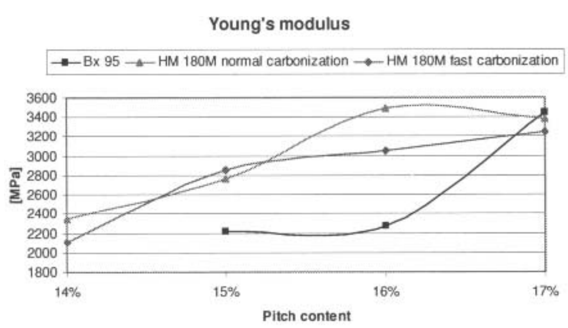

Figure 9: Young's modulus versus pitch content

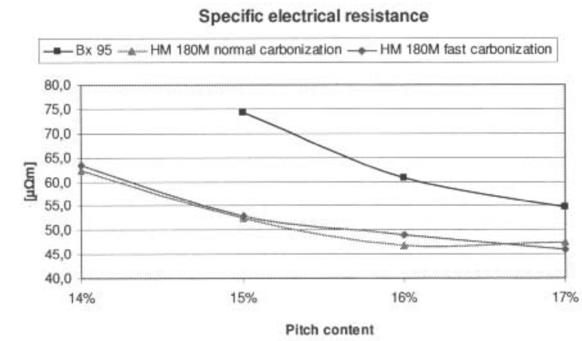

Figure 10: Specific electrical resistance versus pitch content

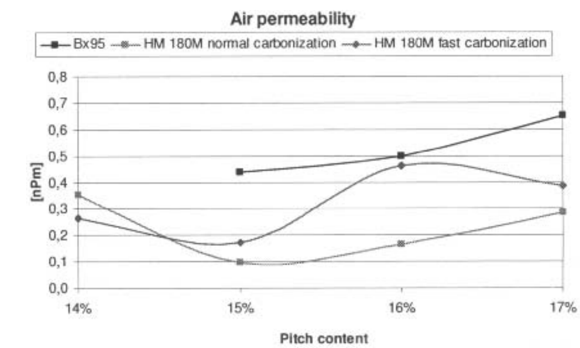

Figure 11: Air permeability versus pitch content

Anode producers put much emphasis on thermal shock resistivity of their anodes. This parameter should be high when the anodes have a high compressive strength and a high Young's modulus. Figures 8 and 9 show these properties for the prepared anodes. If one uses the high-melting pitch both parameters could be raised about 35%.
A very important quality parameter for anode producers is the specific electrical resistance (Figure 10). This parameter should be as low as possible to ensure low energy consumption during alumina electrolysis. This aspect is particular important for new high-amperage pots. For lab scale anodes the use of high softening pitch results in a decrease of the specific electrical resistance by more than 10 %.

The other parameters are commented as follows:

- Air permeability: The higher baked density translates into a lower air permeability of the anode (Figure 11).
- CO_2-reactivity: This parameter is mostly influenced by the characteristics of the coke used for anode production. Therefore there are no big differences detected by using different pitches with the same coke for anode production.

Conclusion

An interesting new property profile of laboratory carbon anodes is achieved by replacing a standard binder pitch by a high softening point binder pitch:

- The baked density of the anode is improved by +0.04 g/cm³
- The specific electrical resistance is lowered by 15 % reducing electricity consumption.
- The pitch content in the anode is reduced from 16 to 15%.
- The pitch toxicity is reduced by 87 %.
- The baking process for the anodes can be expedited because of a lower volatile content in the pitch therefore the throughput of the baking furnace can be raised.

Of particular note is that new high-amperage pots will require anodes of much higher quality and the expected quality improvements associated with the use of high softening point pitches will be appreciated.

Further investigations

Next steps are planned to verify our results on full scale anodes. In addition high softening point pitches will be evaluated for other applications:

- For the production of graphite electrodes (in particular electrode nipples), carbon and graphite cathodes and specialty graphite, high softening point binder pitch would most likely improve the properties of these products significantly. The expected higher density and higher strength may make certain impregnation steps redundant.

- For the production of dolomite and magnesia-carbon refractory bricks the use of high softening point binder pitch would most likely improve the brick properties and may make the tempering process redundant.

Acknowledgement

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Last, but not least we thank EIRICH for their cooperation to introduce the lab scale mixer.

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