Synthetic Alumina Matrix Materials and Binders

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Content

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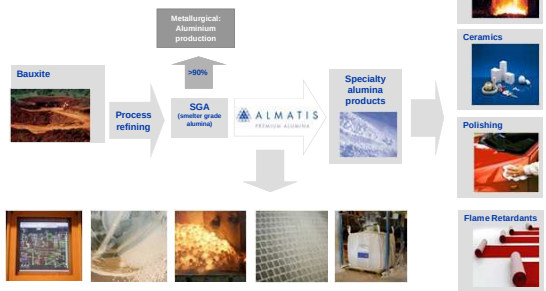
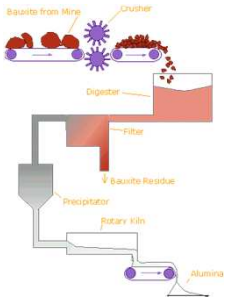
The refining process and the key markets



Bauxite □ synthetic alumina □ applications

Bauxite, Bayer process, and synthetic alumina



Bauxite:

Origin: Australia, Africa, Asia, South America

Mineralogy: $Al(OH)_3$, AlOOH + impurities (Fe_2O_3, SiO_2, TiO_2, Alkalies, Earth alkalies)

Bayer process:

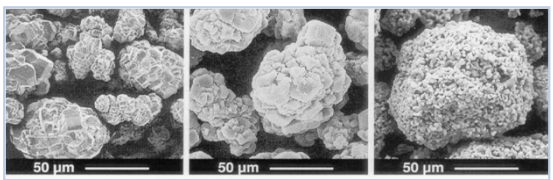
$Al_2O_3 \cdot 3H_2O + 2\ NaOH \rightarrow 2\ NaAlO_2 + 4\ H_2O$

Impurities separated as insoluble “red mud”

Calcination of $Al_2O_3x3H_2O = Al(OH)_3$

Calcination steps:

~ 300℃	Release of chemical bonded water
400 - 500℃	steep increase of specific surface area (~5 auf ~300 m²/g) Activated alumina
1000 - 1200℃	Formation of α-Al_2O_3 (Corundum)



Bauxite for synthetic alumina vs. special refractory bauxite

- "normal" Bauxite for synthetic alumina production = high iron oxide content (30-40%, brown colour, un-calcined material)
- 37 million tonnes Aluminium per year ≈ 75 million tonnes smelter grade alumina ≈ 98 million tonnes $Al(OH)_3$ ≈ 140 million tonnes normal Bauxite as feedstock
- Refractory Bauxite = low iron oxide content (≤ 2% Fe_2O_3 as calcined material) about 1.5 million tonnes per year (mainly China, minor Africa, South America)
- China is dominating the refractory bauxite market, but synthetic alumina is independent from China

High Alumina Cements

Calcium Aluminate Cements (CAC)

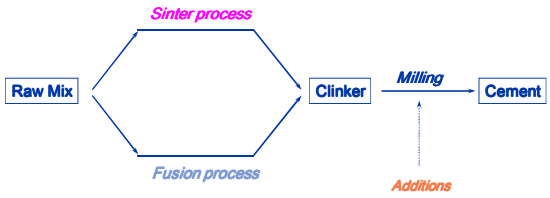
≥ 70% Al_2O_3

≤ 28 % CaO

used as hydraulic binder for refractory castables

for gunning, vibration or self-flowing placement

Production Process types



Mineral phases in High Alumina Cement

C + A

C=CaO (lime) and A=Al_2O_3 (alumina)

C_3A > $C_{12}A_7$ > CA > CA_2 > CA_6

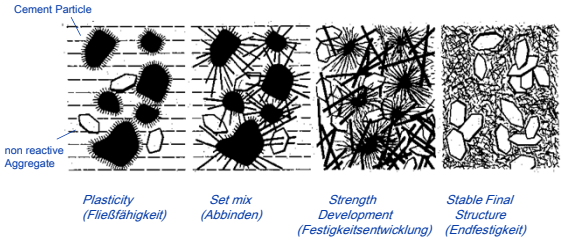
Phases in 70/80% CAC	
Fast Setting	C12A7 (Mayenit)
Moderate Setting	CA
Slow Setting	CA2

Properties of Aluminate Cement phases

Mineral	CaO	Al_2O_3	Melting point (°C)	Density (g/cm³)
C	99.8		2570	3.25/3.38
$C_{12}A_7$	48.6	51.4	1360-1390	2.69
CA	35.4	64.6	1600	2.98
CA_2	21.7	78.3	1750-1765 (decomposition)	2.91
CA_6	8.4	91.6	1875	3.38
α.-A		99.8	2051	3.98

Hydration of cement

Development of Matrix Structure during Hydration Process:



Hydration of cement - temperature and time dependency

Volume change
Base is CAH10

$CA, CA_2, C_{12}A_7 + H_2O$

0 Vol.%:	CAH_{10} (metastable), AH_x (Gel)	< 20°C (time)
- 37 Vol.%	C_2AH_8 (metastable), $AH_{x/3}$ (Gel/cryst.)	20 - 35°C (time)
- 53 Vol.%	C_3AH_6 (stable), AH_3 (cryst.)	> 35°C (drying)

= stable status !

Overview of ALMATIS Calcium Aluminate Cements

80% Al_2O_3 | 70% Al_2O_3

CA 25	CA 14	CA 270	CA 470 TI (NEW)
CA-25 R short CA-25 M medium CA-25 C long	CA-14 W short CA-14 M medium CA-14 S long	2nd generation of 70 % alumina cements	Temperature Independent Cement
Main use in conventio-nal and low cement castables. Fast setting and high early strength develop-ment Dispersion of total mix	Universal use for LC and ULC castables and gunning mixes Optimum flexibility in mix design Additives / alumina must be added	Very low water de-mand with excellent flowability High strength develop-ment No organic additives for full flexibility in product design	For LC and ULC castables using dispersion systems Avoids the ultra long setting time ("never setting") at low tempe-ratures of 5 to 10 °C Additive free

Cement in castables – what happens after installation?

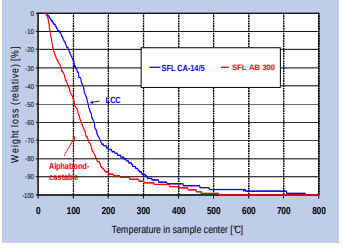
Mixing + Installation	Curing	Drying	Firing
	Min. 24h at room temperature, Optimal >30°C	110°C for 24 h Removal of free or superficial water	200 - 400°C Removal of crystalline water
Grog + CAC + Water + additives	Hydration: Setting Reaction (stiffening of mix) Strength Develop-ment		>1000°C Sintering reaction with other components e.g. CAC + Alumina → CA6

Alphabond – CaO free hydraulic alumina binder

- Soft calcined, re-hydratable alumina
- Alternative to CAC especially for spinel forming, silica fume containing castables
- About 3% recommended for no cement castables (NCC)

	Alphabond 300
Al_2O_3 [%]	91
CaO [%]	<0,1
Na_2O [%]	0,2
SiO_2 [%]	<0,1
Moisture [%] (25 – 250°C)	2,9
LOI [%] (250- 1000°C)	6,0

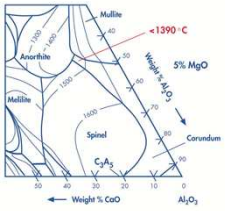
Drying behaviour of CAC and Alphabond



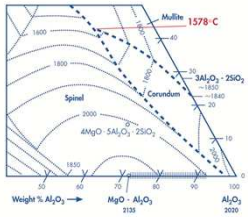
- Low cement castable (5% CA-14)
- Alphabond castable (3% Alphabond)
- Quicker water release of Alphabond in tempe-rature range up to 200°C
- requires more care!

Onset of melting: Spinel forming castables

LCC or ULCC vs. NO-cement castable using Alphabond



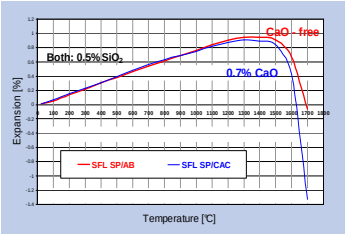
Al_2O_3-SiO_2-MgO-CaO



Al_2O_3-SiO_2-MgO

Thermomechanical properties of Spinel forming castables

Alphabond (NCC) vs ultra low cement castable (ULCC)



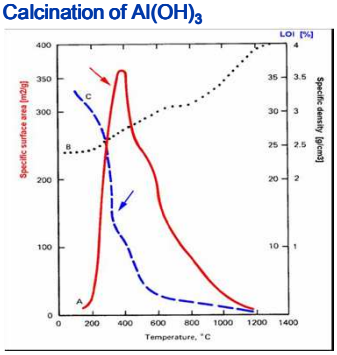
- $T_{0.5}$ of NCC is 40-50°C higher than for ULCC (2.5% CAC)

Even more pronounced difference should be expected in LCC – systems (5% CAC) with about 1.5% CaO

Samples pre-fired 1500 °C/5h

Matrix aluminas: Calcined and reactive aluminas

Calcination of $Al(OH)_3$



Calcination is usually done in two steps:

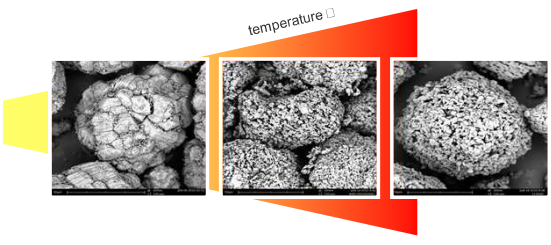
1. Flash calciner for de-watering
2. Rotary kiln for controlled
   - surface area
   - crystal growth
   - phase control

2. calcination step done by Almatis → here is the quality created!

Calcined alumina products for all markets:

- Refractory
- Ceramics
- Polishing

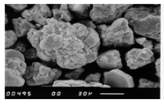
Conversion of alumina



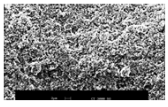
Milling of matrix aluminas

- Calcined and reactive aluminas must be ground before being used in refractory applications

before



after



- Continuous mills (with air classification)
  - partially ground product
- Batch mills → fully ground product

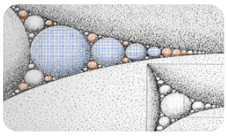
Calcined and reactive alumina

Characterisation:
- Soda content (Na_2O)
- Sintering reactivity
- Primary crystal size
- Specific surface area

Fineness
- Unground (UG)
- Ground (G)
- Fine Ground (FG)
- Super Ground (SG)

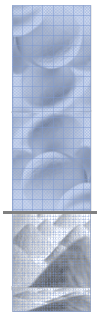
Calcined and reactive alumina in refractories

Calcined aluminas (or aggregate fines)
- Similar particle size to ground mineral aggregate
- Silica fume or sub-micron "reactive" alumina are needed to fill the voids



Reactive aluminas
- Alumina <1 µm e.g. RG 4000 can replace silica fume as sub-micron filler
- Reduce significantly the required liquid to achieve high flowability
- Almost all modern high performance monolithic refractories contain significant amounts of reactive alumina

Castable formulation



Aggregates

Fraction > 45 µm
65-75 %

-The brick to build the foundation (Coarse)
- Filling the intermediate voids between the coarse aggregate (Fine)

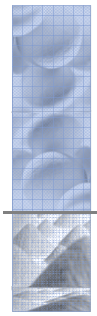
Matrix products

Fraction < 45 µm
25-35 %

Significant influence on:
Rheology, Workability, water demand, strength development

- Fill the micron size voids without adding excess liquid
  - Amount impacts rheology: vibration, self flow, pumpable
  - Size distribution can cause dilatant or shear thinning behaviour
- Binders hold it together until thermal sintering occurs
- Additives
  water reducing: dispersants, deflocculants, plasticizers
  Set controlling: retarders, accelerators

Castable formulation



Aggregates

Fraction > 45 µm
65-75 %

- Tabular Alumina
- Spinel
- Bonite
- Others

Matrix products

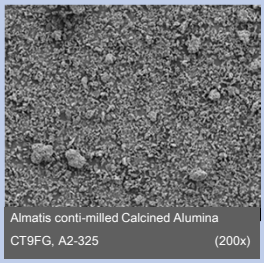
Fraction < 45 µm
25-35 %

Significant influence on:
Rheology, Workability, water demand, strength development

- Calcined and Reactive Alumina
- Tabular-,Spinel-,Bonite- fines
- Calcium Aluminate Cement
- Alphabond
- Dispersing Alumina
- Other fines

Matrix alumina: Ground calcined alumina

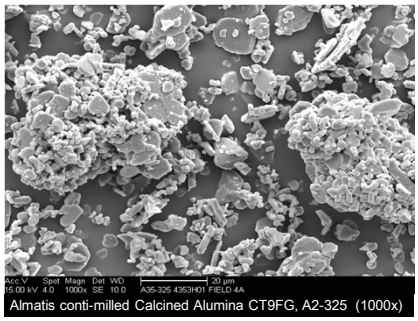
Continuous ball milled (partially ground) aluminas



Almatis conti-milled Calcined Alumina
CT9FG, A2-325 (200x)

- A high use material in brick and early low cement castables
- Significant >20 micron agglomerates
- Agglomerates have significant open porosity – absorbs water
- Similar particle size to ground aggregate minerals
- Silica fume or a sub-micron "reactive" alumina are needed to fill the voids <2 micron for low water LCC's and ULCC's

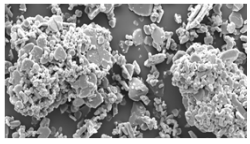
Ground calcined alumina

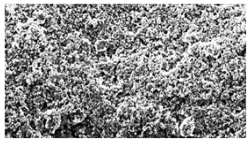


Almatis conti-milled Calcined Alumina CT9FG, A2-325 (1000x)

- Some 30 µm agglomerates
- Particles >10 µm are porous

Calcined alumina / reactive alumina





- Partially ground alumina
- Porous agglomerates >20 µm
  - absorb water
  - reduce reactivity

- Fully ground alumina
- Single crystals
- Minimal unground agglomerates coarser than >20 µm
- High amount of <3 µm particles

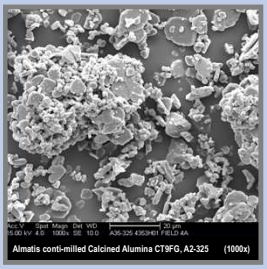
Matrix alumina: Reactive alumina

Batch ball milled (fully ground) aluminas "reactive aluminas"

- Minimal unground agglomerates – little water absorption
- Minimal >20 micron particles & significant <3 micron particles
- Significantly finer than ground aggregate minerals
- Typically combined with ground aggregate fines (T60/T64 <45 µm) or possibly < 45 µm ground calcined alumina to fill out the matrix particle distribution

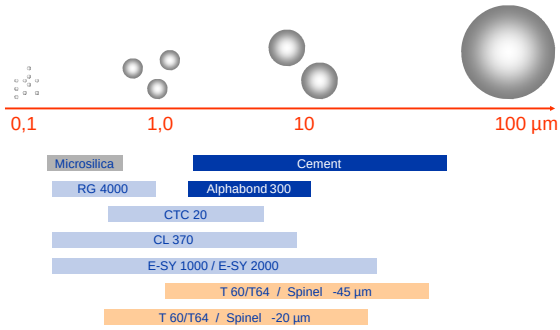
- Significantly reduces the liquid requirement to achieve high flowability in low cement and ultra low cement castables
- <1 micron alumina can replace silica fume as sub-micron filler
- Almost all modern high performance monolithic refractories contain significant amounts of reactive alumina

Why Ground Aggregate vs Calcined Alumina?



<45 micron (-325 mesh) ground calcined aluminas have been replaced with tabular alumina fines in many high performance monolithic refractories

Particle size distribution (PSD) - matrix concepts



Particle size distribution (PSD) - matrix concepts

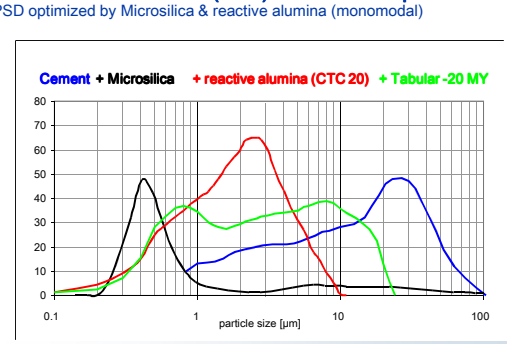
4 cases for vibratable castables

Cement PLUS .....

Fraction	Component	Product
< 1 µm	monomodal micro fines	Microsilica or Reactive Alumina RG 4000
0.5-10 µm	monomodal medium fines	Reactive Alumina CTC 20
0.5-20 µm	densification by sintered aggregate	Tabular Alumina T-60/T-64 -20 µm Spinel AR78 -20 µm
<1- 10 µm:	bimodal micro + medium fines	Reactive Alumina CL 370

Particle size distribution (PSD) - matrix concepts

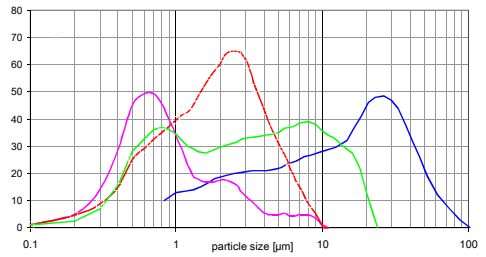
PSD optimized by Microsilica & reactive alumina (monomodal)



Particle size distribution (PSD) - matrix concepts

PSD optimized by 2 reactive alumina (monomodal)

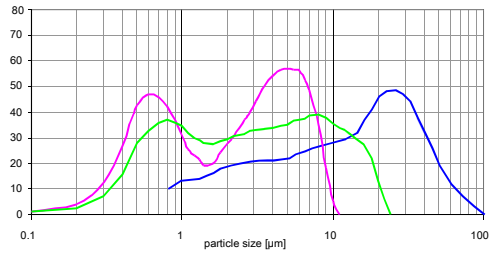
Cement + reactive alumina (RG 4000) + reactive alumina (CTC 20) + Tabular -20 MY



Particle size distribution (PSD) - matrix concepts

PSD optimized by 1 reactive alumina (bimodal)

Cement + reactive alumina (CL370) + Tabular -20 MY



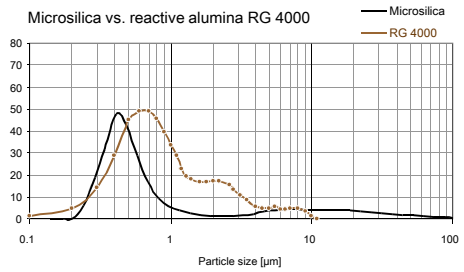
Particle size distribution (PSD) - matrix concepts

… to show similarities or differences of:

1) Microsilica & Reactive Monomodal Alumina RG 4000
   both represent ultrafines below 1 µm
2) Microsilica & Reactive Alumina E-SY 1000
   both represent ultrafines below 1 µm
3.a) Cement CA-14 & Tabular Alumina T-60/T-64 -45 MY
   can be replaced by one another to reduce cement amount or increase density
3.b) Cement CA-14 and Alphabond
   different PSD of binders needs revised design of matrix fines

Particle size distribution (PSD) - matrix concepts

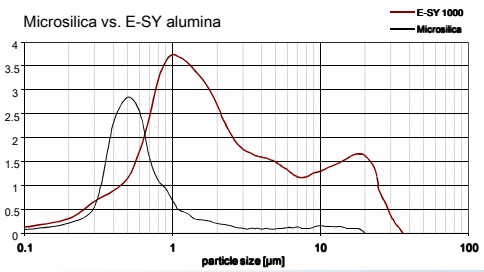
Case 1) ultrafine fraction below 1 µm



Density difference must be considered for exchange:
SiO_2 glass ≈ 2.3, α-Al_2O_3 3.99 g/cm³

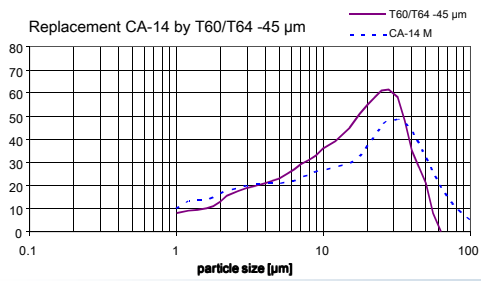
Particle size distribution (PSD) - matrix concepts

Case 2) ultrafine fraction below 1 µm – microsilica free castables with E-SY
but…E-SY 1000 covers a wider range of PSD fines and a replacement of microsilica by E-SY requires some more modifications



Particle size distribution (PSD) - matrix concepts

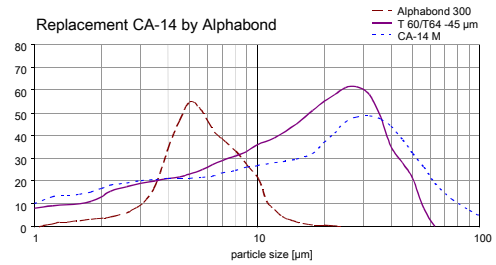
Case 3a) cement replacement by aggregate (T60/T64; Spinel) -45 µm
together with T60/T64 -45µm some 0-0.2 mm should be added



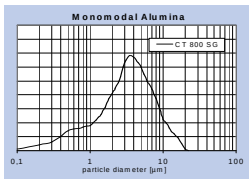
Particle size distribution (PSD) - matrix concepts

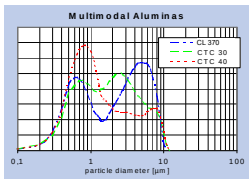
Case 3b) Replacement CA-14 by Alphabond

- replacing cement by Alphabond needs revised PSD design, e.g. by increasing T60/T64 -45µm proportion



Reactive Alumina for high performance castables

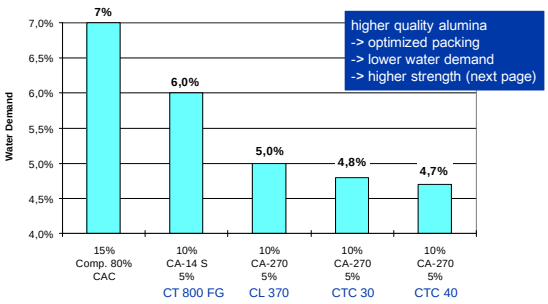




Product	CT 800 SG	CL 370	CTC 30	CTC 40
BET surface area [m²/g]	1.0	3.0	3.8	4.8
d_{50} CILAS [µm]	3.4	2.5	1.5	1.2

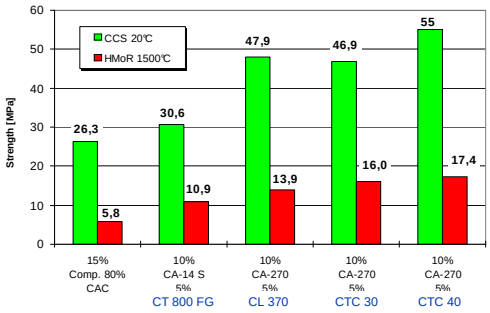
- Increase of sinter reactivity
- Higher surface area
- lower d_{50}

Improvement of medium cement castable

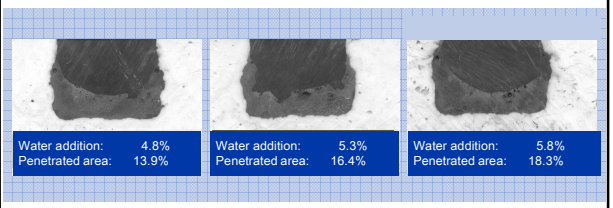


higher quality alumina
-> optimized packing
-> lower water demand
-> higher strength (next page)

Improvement of medium cement castable



Crucible slag test – different mixing water content



Water addition:	4.8%	
Penetrated area:	13.9%	
Water addition:	5.3%	
Penetrated area:	16.4%	
Water addition:	5.8%	
Penetrated area:	18.3%	

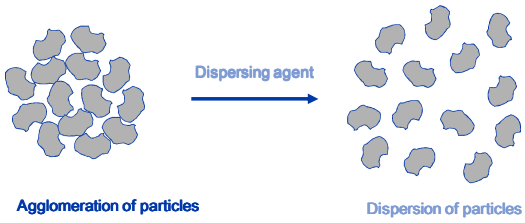
Source: EU steel plant
Pre-fired to 1400°C
Slag test 4 hours @ 1560°C

More water
higher infiltration of slag
1% water ≈ 3% open porosity!

Matrix aluminas in refractories

- Improved refractoriness by increasing overall alumina content of formulations using natural raw materials
- Better particle packing resulting in higher mechanical strength and abrasion resistance
- Formation of a high refractory matrix by reacting with binder components like calcium aluminate cement and / or clays.

Dispersion of fine components in the castable matrix



Target: separate / de-agglomerate particles and obtain better flowability at reduced water demand

Dispersing Alumina - major function

Dispersion of fines (Aluminas, Cement, Microsilica…)
- ADS 1, ADS 3, ADW 1 for microsilica free castables
- M-ADS 1, M-ADS 3, M-ADW 1 for microsilica containing castables

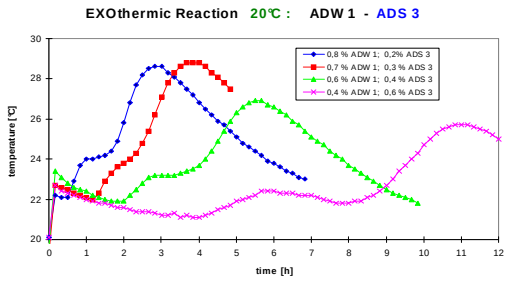
Reduction of mixing water demand

Control of setting
- Retard setting (S-Types)
- Accelerate setting (W-Types)

Control of placement and setting behavior at low and high temperatures

Evenly distribution in the dry mixed castable (Σ 1% addition)

Dispersing alumina - continued



Dispersing alumina – setting control

Self flowing tabular low cement castable

Different Temperatures + Dispersing Alumina combinations
- Exothermic Reaction Times

Test	#	0	1	2	3	4	5	6	7	8	9	10	11
Test Temp.	°C	3	7	7	20	20	20	20	20	20	35	35	35
ADW 1	%	1	1	0,5	0,8	0,2	0,8	0,7	0,6	0,4	0,5	0,2	0,1
ADS 1	%	-	-	0,5	0,2	0,8	-	-	-	-	-	-	-
ADS 3	%	-	-	-	-	-	0,2	0,3	0,4	0,6	0,5	0,8	0,9
EXO Start	h	2,9	1,1	2,7	0,5	1,0	0,6	1,2	2,1	4,2	0,2	1,7	2,6
EXO Max	h	13	7,3	18,7	2,0	6,9	2,9	3,8	5,6	11,1	1,6	3,4	5,2

Note: EXO start -> correlates with working time/flow stop
EXO max -> correlates with strength development/demoulding time

Note: ADS 3 alone gives never setting!!

Matrix concepts for alumina castables