Calcium Aluminate Cement
Matrix Aluminas
Dispersing Aluminas

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Production of synthetic alumina

High alumina cement

Matrix aluminas: Calcined and reactive aluminas

Dispersing aluminas


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The refining process and the key markets
Metallurgical: Aluminium production
>90%
Bauxite
Process refining
SGA (smelter grade alumina)
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Specialty alumina products
Refractories
Ceramics
Polishing
Flame Retardants
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Bauxite → synthetic alumina → applications
Courtesy PaHaGe
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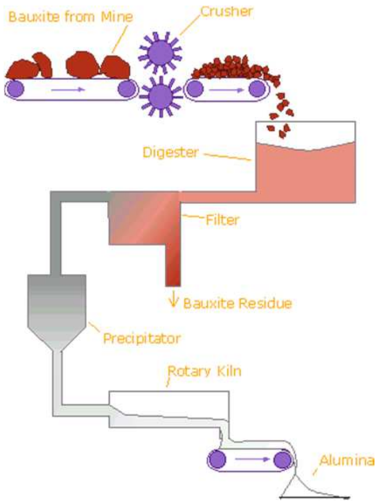
Bauxite, Bayer process, and synthetic alumina



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:

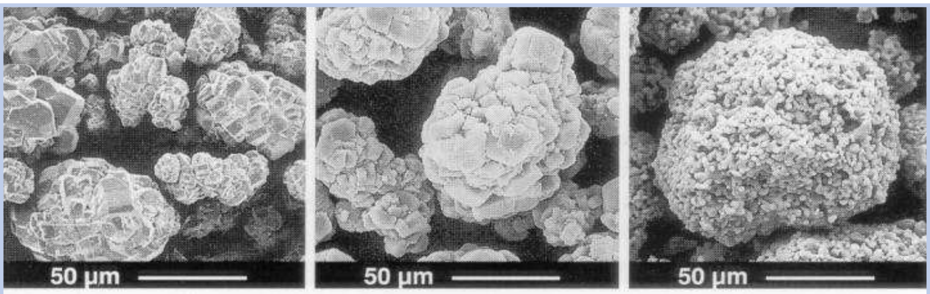
$Al_2O_3 \cdot 3H_2O + 2\ NaOH \rightarrow 2\ NaAlO_2 + 4\ H_2O$

Impurities separated as insoluble “red mud”

Calcination of $Al_2O_3x3H_2O = Al(OH)_3$

Calcination steps:

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



Metallurgical vs. refractory bauxite

Metallurgical bauxite

- Production: > 200 million t/a
- Composition: Al_2O_3: 40-50% ; Fe_2O_3: 30-40%
- Used for: Aluminum and alumina production
  2,5 million t/a specialty alumina e.g. tabular, WFA, calcined alumina, CAC
- Sources: worldwide

Refractory bauxite

- Production: < 10 million t/a
- Composition: Al_2O_3: > 80% ; Fe_2O_3: < 2
- Used for: Refractories, abrasives, other
  2,2 million t/a Sintered bauxite, 1 million t/a BFA
- Sources: China, Guyana (others)

China is dominating the refractory bauxite market, but synthetic alumina is independent from China. For aluminium (alumina) production, China is a big importer of Bauxite!

High Alumina Cements

Calcium Aluminate Cements (CAC)

$\geq$ 70% Al_2O_3

$\leq$ 28 % CaO

used as hydraulic binder for refractory castables

for gunning, vibration or self-flowing placement

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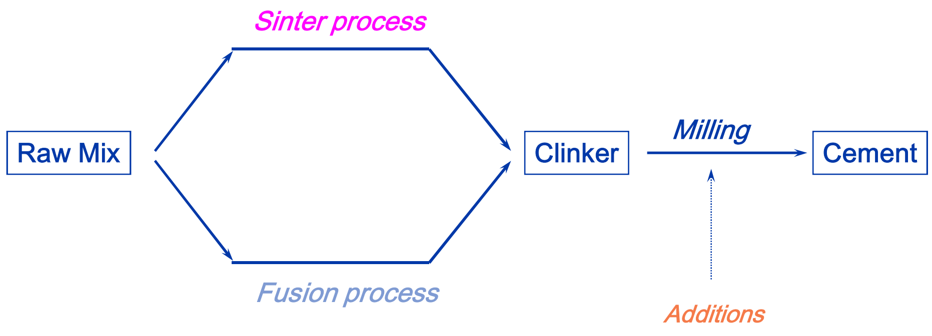
Production Process types



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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	$C_{12}A_7$ (Mayenit)
Moderate Setting	CA
Slow Setting	CA2

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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

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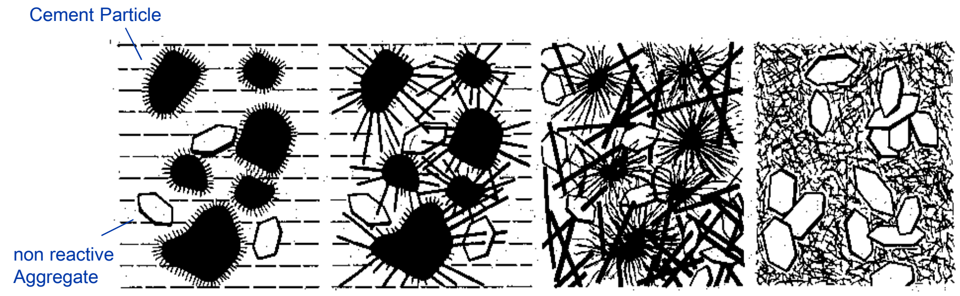
Hydration of cement

Development of Matrix Structure during Hydration Process:



Plasticity (Fließfähigkeit)

Set mix (Abbinden)

Strength Development (Festigkeitsentwicklung)

Stable Final Structure (Endfestigkeit)

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

NEW

CA 25

CA-25 R short
CA-25 M medium
CA-25 C long

- Main use in conventional and low cement castables.
- Fast setting and high early strength develop-ment
- Dispersion of total mix

CA 14

CA-14 W short
CA-14 M medium
CA-14 S long

- Universal use for LC and ULC castables and gunning mixes
- Optimum flexibility in mix design
- Additives / alumina must be added

CA 270

2nd generation of 70 % alumina cements

- Very low water demand with excellent flowability
- High strength develop-ment
- No organic additives for full flexibility in product design

CA 470 TI

Temperature Independent Cement

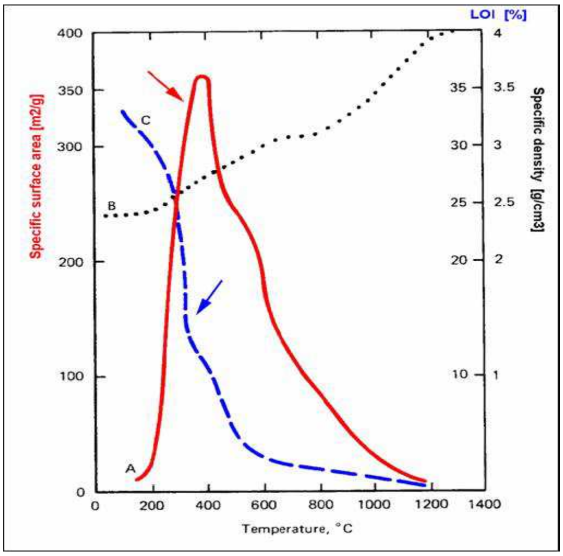
- For LC and ULC castables using dispersion systems
- Avoids the ultra long setting time ("never setting") at low tempe-ratures of 5 to10 °C
- Additive free

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 Development	However, in high density LCC & ULCC free water not completely removed at 110°C!	>1000°C Sintering reaction with other components e.g. CAC + Alumina → CA6

Matrix aluminas:
Calcined and reactive aluminas

Calcination of $Al(OH)_3$



Calcination is usually done in two steps:

1. De-watering in flash calciners or rotary kilns

2. Rotary kiln for controlled
   - surface area
   - crystal growth
   - phase control

2. calcination step → here the quality is created!

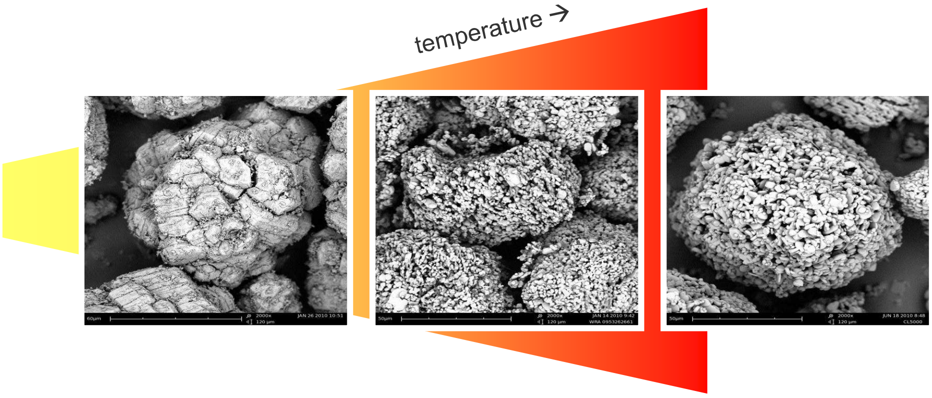
Calcined alumina products for all markets:

Refractory

Ceramics

Polishing

Conversion of alumina



Calcined and reactive alumina

Characterisation:

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

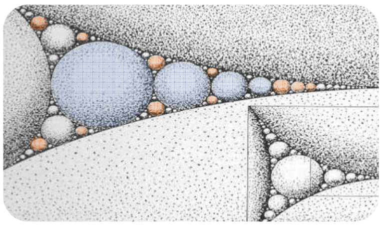
Fineness

- Unground (UG) ≈ 100µm
- Ground (G) ≤ 63µm
- Fine Ground (FG) ≤ 45µm
- Super Ground (SG) ≤ 20µm

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

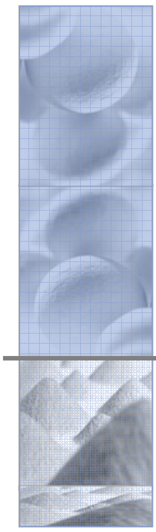


Reactive aluminas

- 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 perfor-mance 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

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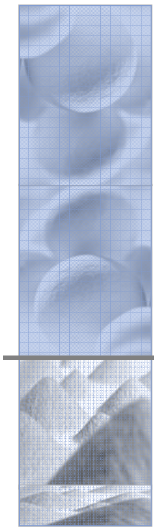
Castable formulation



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

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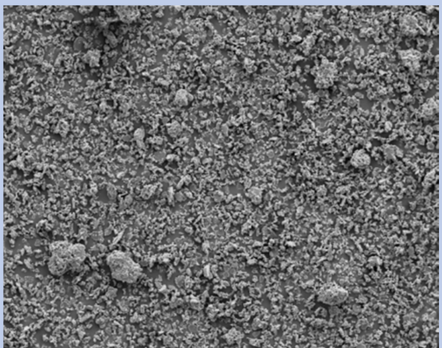
Matrix alumina: Ground calcined alumina

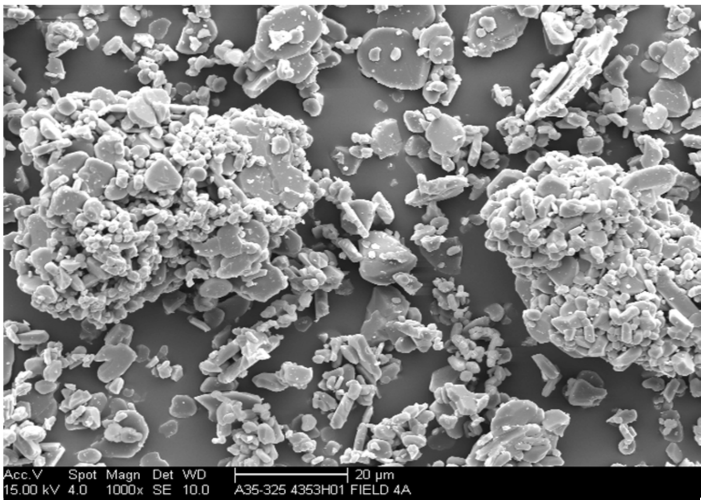
Continuous ball milled (partially ground) **aluminas**



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

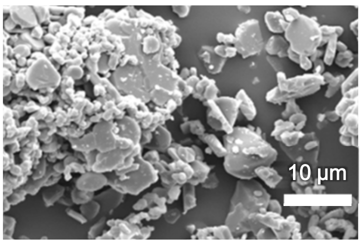
Ground calcined alumina



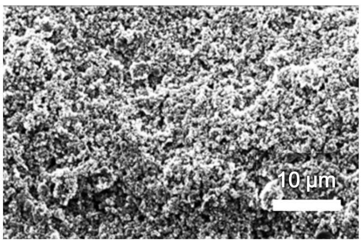
Almatis conti-milled Calcined Alumina CT9FG, A2-325 (1000x)

- 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

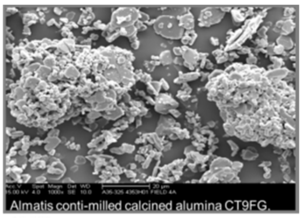
Matrix alumina: Reactive alumina

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

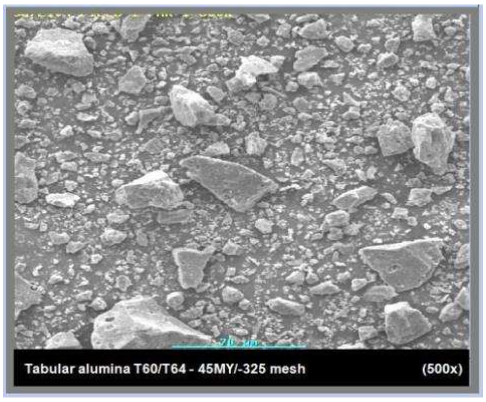
- Minimal unground agglomerates – little water absorption
- Minimal >20 micron particles & significant <3 micron particles
- Significantly finer than ground aggregate minerals
- Typically combined with ground aggregate fines (T60/T64 <45 µm) or possibly < 45 µm ground calcined alumina to fill out the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

Ground calcined alumina vs. Tabular alumina -45MY



Residual agglomerates absorb mixing water



Replacement of calcined alumina with Tabular alumina -45 MY reduces water demand and open porosity after drying

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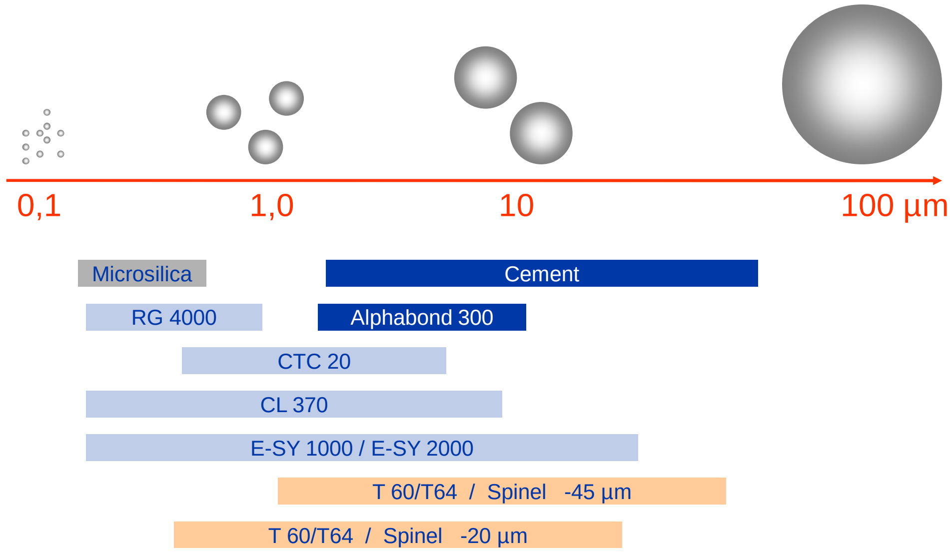
Particle size distribution (PSD) - matrix concepts



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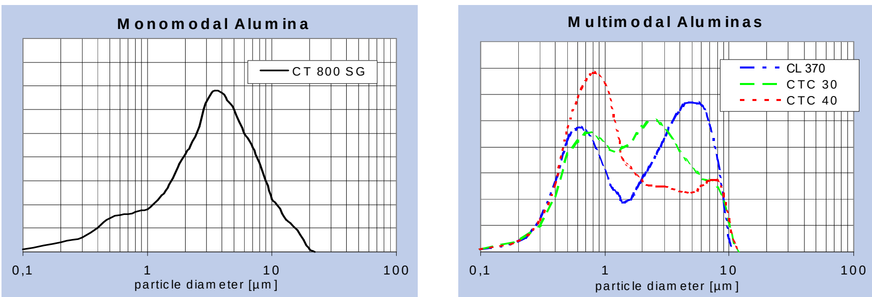
Reactive Alumina for high performance castables



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}

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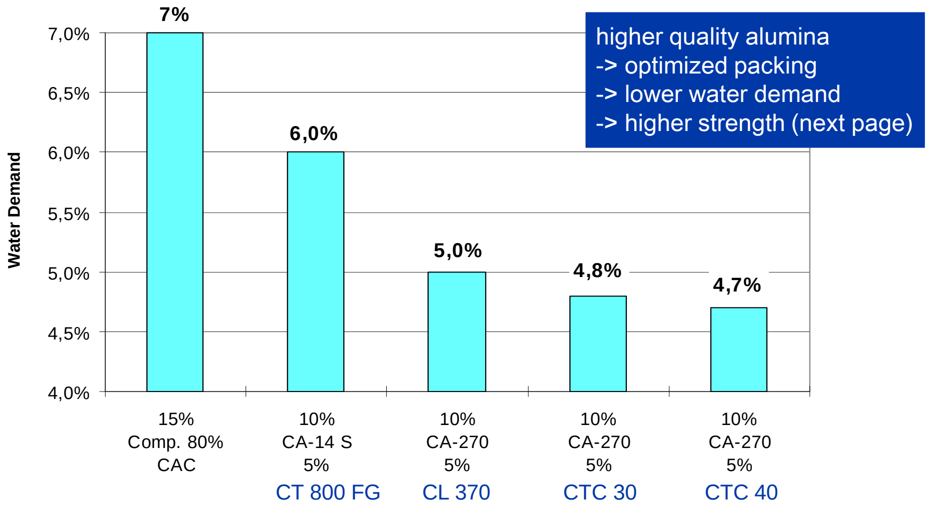
Improvement of medium cement castable



Think alumina, think Almatis.

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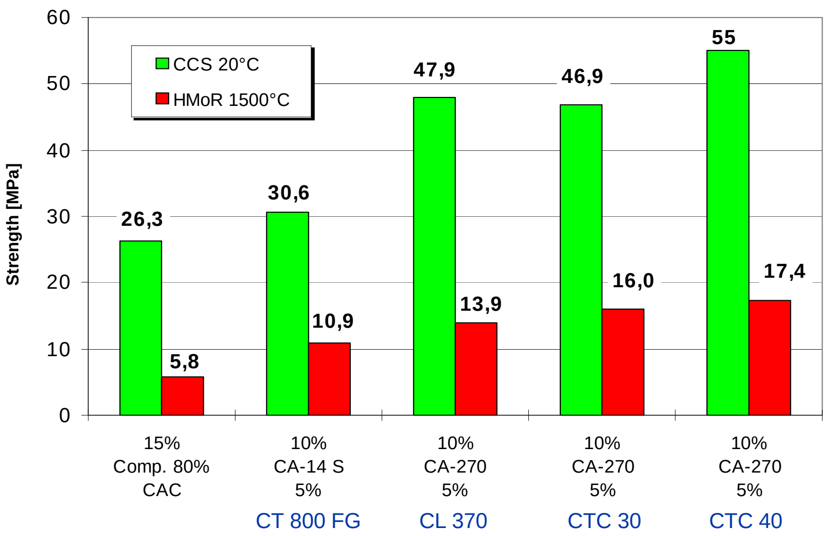
Improvement of medium cement castable



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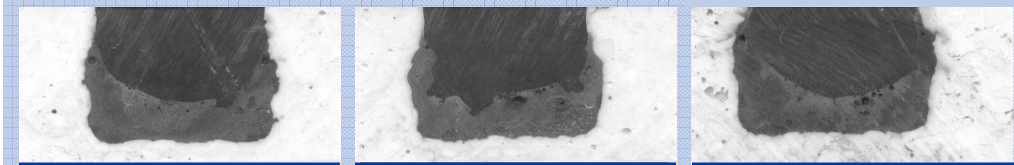
Crucible slag test – different mixing water content



Water addition: 4.8%	Water addition: 5.3%	Water addition: 5.8%
Penetrated area: 13.9%	Penetrated area: 16.4%	Penetrated area: 18.3%
Cold Crushing Strength:40MPa	Cold Crushing Strength:32MPa	Cold Crushing Strength:20MPa

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

Agglomeration of particles

Dispersion of particles

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

Dispersion of fines - Dispersion principles

Electrostatic Dispersion:

Dispersing agent “docks” with its negative charge on particle surface, particles mutually repulse

- Example: Ligninsulfonates, Na-citrate

Steric Dispersion:

Usually long chain polymers, covering surface and keep distance between particles

- Example: Polyacrylates

Electrosteric Dispersion:

Combines electrostatic and steric effect, polymer chains with negative charge

- Example: high performing polymers

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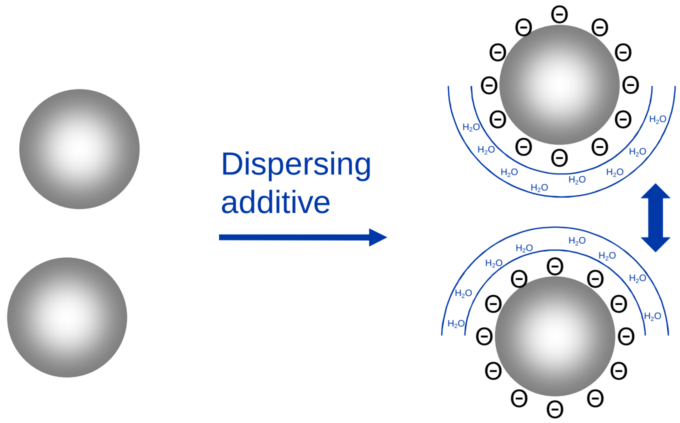
Dispersion of fines - Dispersion principles
Electrostatic Dispersion



Identical surface charge → Repulsion

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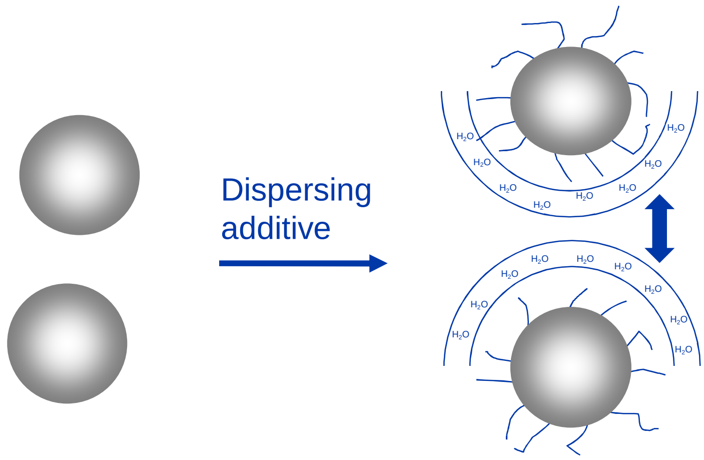
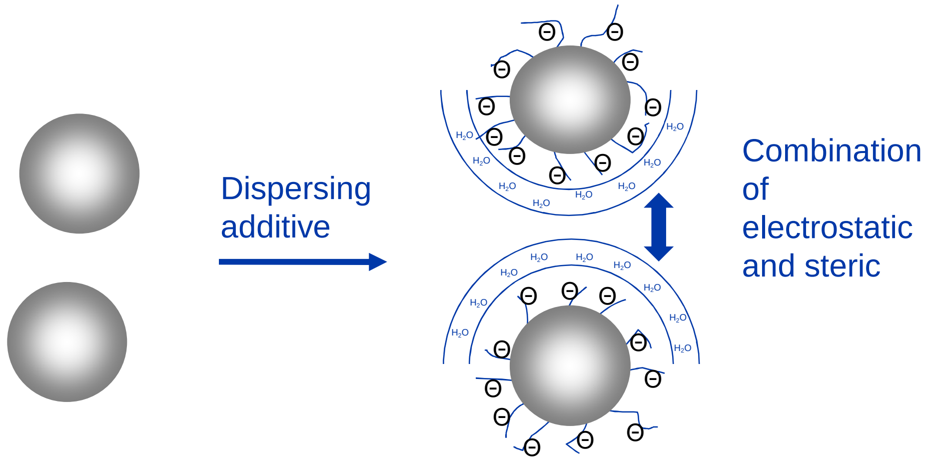
Dispersion of fines - Dispersion principles
Steric Dispersion



Polymer chains spread particles distance

Dispersion of fines - Dispersion principles

Electrosteric Dispersion



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

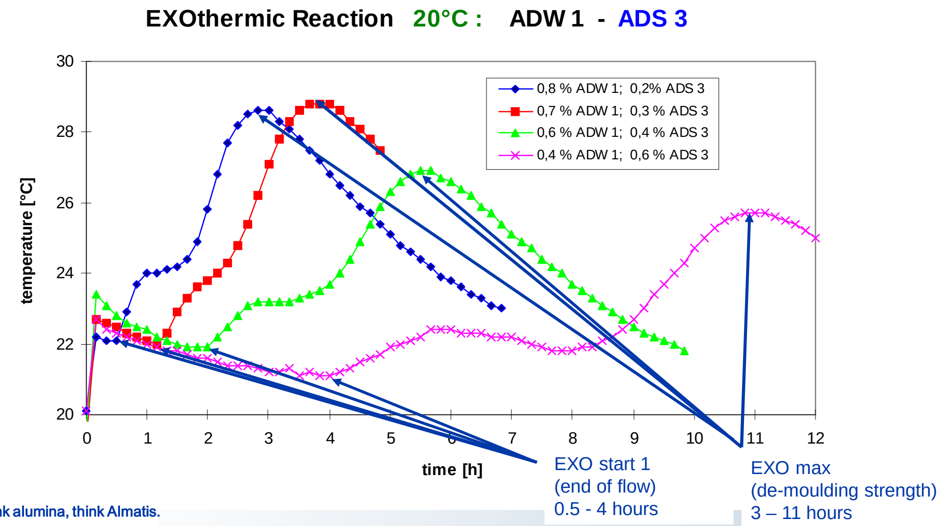
Control of setting

- 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 (∑ 1% addition)

Dispersing Aluminas – example ADS/W



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!!

Setting and strength development

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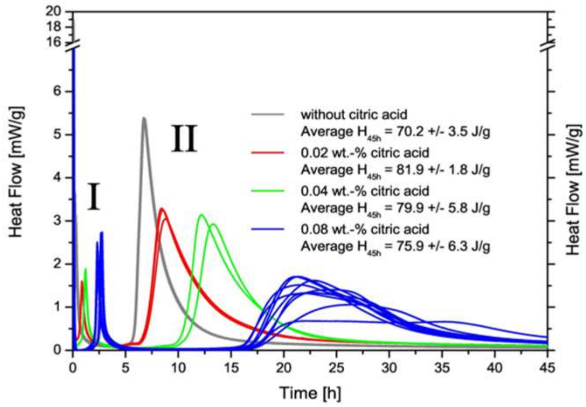
Calorimeter testing: cement paste with polyphosphate + 0 – 0.08% citric acid



I Reaction phosphate/cement → stiffening, no setting start
moderate retardation by citric acid

II Main cement reaction and strength development
strong retardation by citric acid, weaker and broader peak

Phosphate additive – fake hardening

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Cup setting test used in the industry

- Easy test, but dangerous with phosphate additives
- First “hardening” or stiffening is NOT cement setting reaction!
- Only very low strength developed (CCS < 1 MPa)
- Movement or demoulding of cast pieces too early:
  - Micro-cracks (visible only after drying or firing)
  - Slumping of large on-site installations when demoulding

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Castable additive systems: Cost of safety

- Castables are tailored to individual on-site conditions
  - Additive system
  - Optimum dosage
- Dispersing alumina dosage of 0.7 – 1% (ULCC, LCC) ensure correct dosage and easy use
- Traditional additives added in small amounts (0.05 – 0.2% for phosphate/citric acid)
- Small deviations in citric acid addition (imprecise dosing / homogenisation) have strong impact on
  - Placing properties
  - Setting behaviour
- Risk to impair performance of the castable is high

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Castable additive systems: Cost of safety

- Incorrect dosage
  - → might be identified by QC testing
  - → re-adjustment
  - → re-production
- Bag to bag variations due to poor homogenisation
  - → difficult to detect
  - → problems during installation
- Short term aging caused by citric acid
  - → installation takes longer than scheduled
  - → sagging (former removed too early)
  - → conflicts with upcoming R & M activities
  - → non-availability of aggregate, bottleneck in production

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Castable additive systems: Cost of safety

- Retarded strength development
  - → Microcracks during de-moulding
  - → Visible after drying / firing
  - → Scrap in precast shape manufacturing
  - → Reduction of lining life
- Installation failures cause complaints and costs
  - → Additional quality control
  - → Complaint handling
  - → Reproduction of material
  - → Production downtime at the end user (worst case)
  - → Bad reputation and potential loss of business
- Reliable setting behaviour (M-ADS/W) is essential for
  - smooth installation
  - low complaint rate
  - low risk of high unanticipated costs

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Conclusion castable additives

- Phosphate based additive systems are low cost solutions compared to dispersing aluminas. Disadvantages:
  - Control of working time and strength development
  - Sensitivity to slight over-dosages of citric acid
  - Lower storage stability
- Silica fume quality/content influence workability/setting
- Dispersing aluminas provide much more robust system for reliable castable performance and smooth installation

Higher price of modern solution M-ADS/W or ADS/W

→ best cost/performance ratio