HÜTTENES-ALBERTUS
Chemische Werke GmbH

Advances in alkaline phenolic resole resins

SINOTHERM® - AN OVERVIEW

Ian Harris Nov 2010

R 8.2.

TABLE OF CONTENTS

SINOTHERM® - PROCESS

Latin: No - Temperature (No Bake) Process

2.1. HISTORY

- The Alpha Set Process was patented by BORDEN UK in 1983.

- The Alpha Set, also called **ECP Process**, is one of the many No Bake processes:

Inorganic sodium silicate	1952
Furan No Bake (FNB)	**1958**
Phenolic No Bake, acid cured	**1958**
Alkyloil Urethane No Bake	1965
Phenolic Urethane No-Bake (UNB)	**1970**
Inorganic Phospate No Bake	1974
Amine Polyol Urethane No Bake	1978
Polyether Polyol Urethane No Bake	1980
Alkaline Phenolic No Bake	**1983**

- Of which ECP process was the latest “new” system

2.1. CHEMISTRY (1)

- A phenolic, water based resin which reacts with a co-reactant, ester to form a cross linked phenolic resin.
- With the heat from the casting a secondary cure occurs that leads to a thermal cured phenolic binder.

Resin	Ester Hardener
- Aqueous, phenolic Resole	- Blend of diff. aliphatic Esters
- Highly alkaline nature	- Non toxic
- Sodium-, Potassium- , or mixed (hybride) systems	- Non corrosive
- Low free Formaldehyde	- Many additives known
- Low free Phenol	- Different Esters to adjust cure speed
- Low Nitrogen content < 1%	

2.1. CHEMISTRY (5)

CURING CHEMISTRY

Phenolic Resin + Ester

↓

Cured Binder

(Initial Cure)

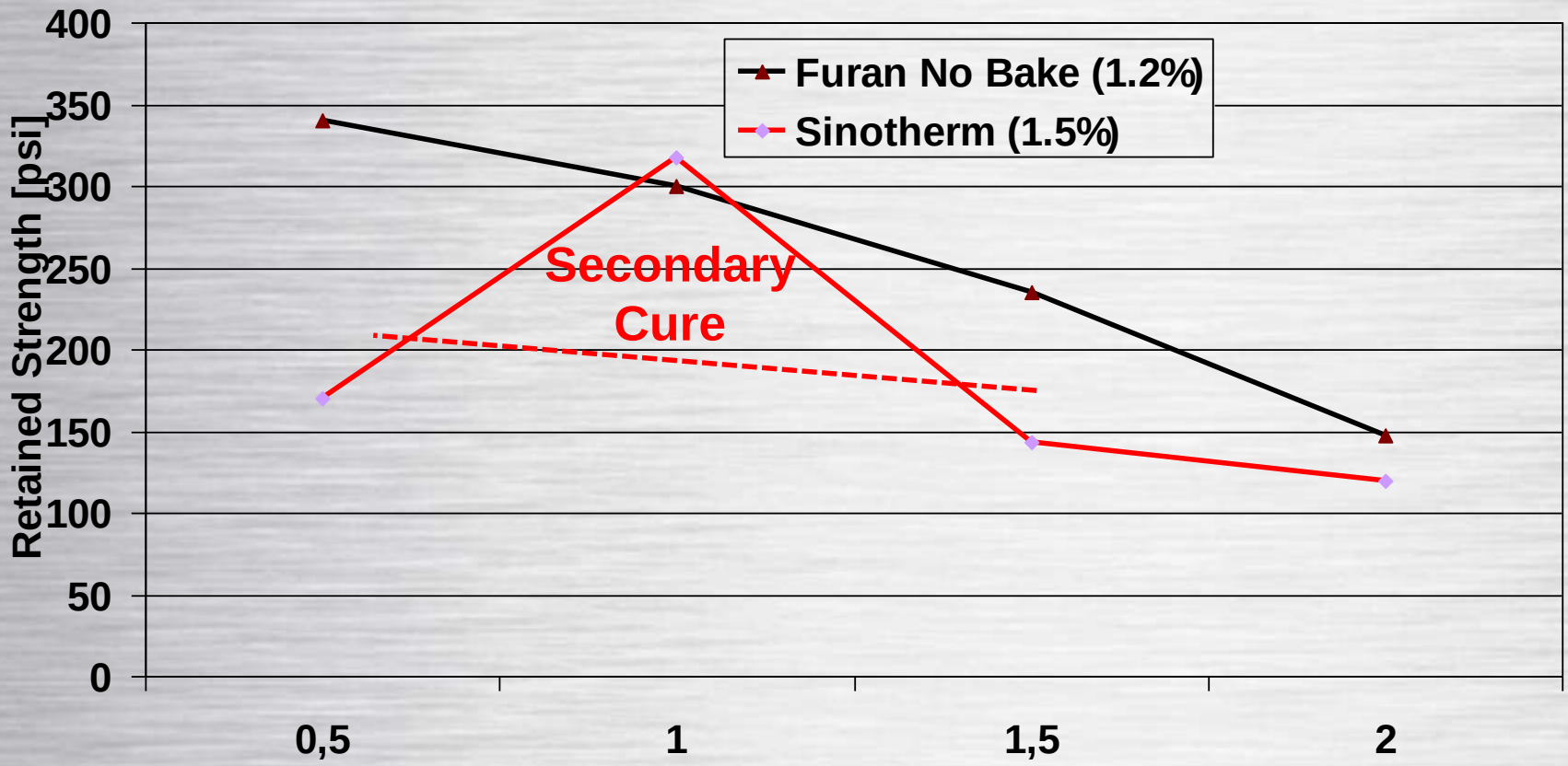
↓ Casting Temperature

Cured Binder

(Secondary Cure)

2.1. CHEMISTRY (6)

HOT STRENGTH COMPARISON: SINOTHERM vs. FURAN RESINS



Conditions: 1800°F/50psi (980 °C/3,45 bar) compressive load

2.2. PRO´S AND CON´S OF SINOTHERM (1)

- **ADVANTAGES**
  - Can be used with all types of sand
  - Very low nitrogen and no sulfur
  - Low odour at coremaking and casting
  - Water based - therefore low VOCs
  - Easy draw and pattern release
  - High hot strength
  - Reduced hot tears and expansion defects
  - Less cleaning costs, less scrap
  - Easy shakeout

2.2. PRO´S AND CON´S OF SINOTHERM (2)

- **DISADVANTAGES**
  - Slower strength development than PUNB & Furan
  - Lower ultimate strength than acid set Furan or Phenol systems; but: Secondary Cure!
  - Limited shelf life of resins (1-6 months, depending on type and temperature)
  - Higher benzene emission after casting with old type of Sinotherm systems
  - Sand reclamation levels are lower than with Furan No Bake
    - higher disposal costs.

2.3. USAGE (1)

- **SINOTHERM USAGE**
  - Sinotherm can be used with all alloys. It is perfect for steel, nodular iron and aluminum castings
  - Binder levels are dependant on substrate, casting size, & closing system used. Average addition rates are typically between 1,0 - 1,8% b.o.s.
  - Ester levels vary in the range from 20-25% b.o.r.
  - The best working temperature is between 20-30 °C, but can be from -10-45 °C with special part II´s.
  - Curing time can be adjusted by blending different hardeners using an Ester blender systems.
  - Alcohol and water based coatings can be used

2.3. USAGE (2)

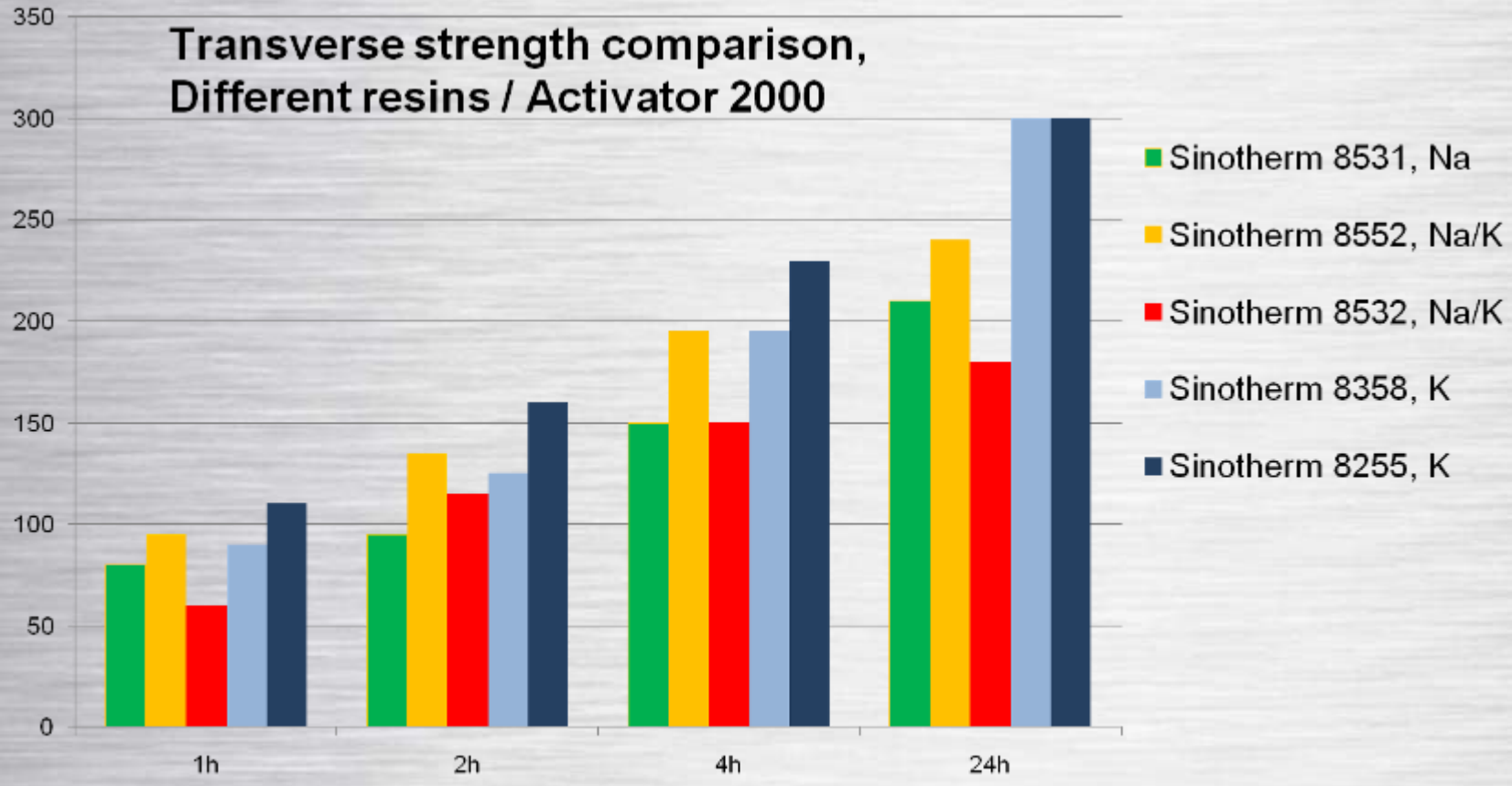
- **PRODUCT SELECTION CRITERIA**
  - **Resin and Hardener:**
    - Work/Strip time ratio/requirement
    - Flask- or flaskless moulding?
    - Hand- or automated moulding?
    - Type and quality of sand
    - Environmental restrictions
    - Mixed sand costs
    - Climate and shelf life requirements
  - **Coating:**
    - Application of coating

2.3. USAGE (3)

With the right Sinotherm System anything from big to intricate and small castings can be manufactured

2.3. USAGE (4)

SINOTHERM – Part I Comparison



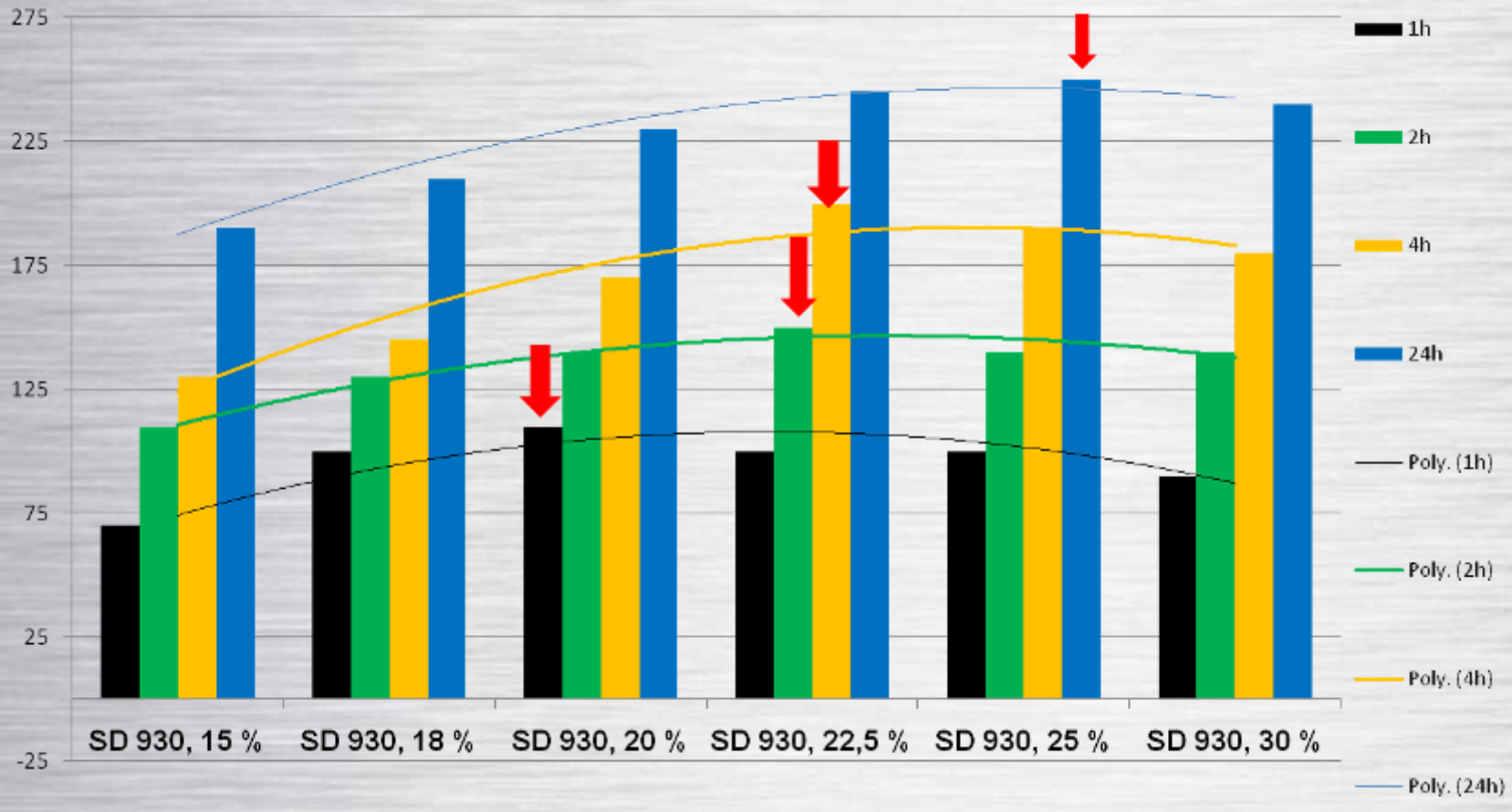
Green: Sodium

Yellow/Red: Hybrid

Blue: Potassium

2.3. USAGE (5)

SINOTHERM USAGE – Part II Optimization



Sinmotherm 8358 1,5%, Sand H32 tested with Activator 2000

2.4. TESTING METHODS

USA

GERMANY

ASIA

2.5. SUBSTRATES AND RECLAMATION (1)

- **Substrates and Resin Level**

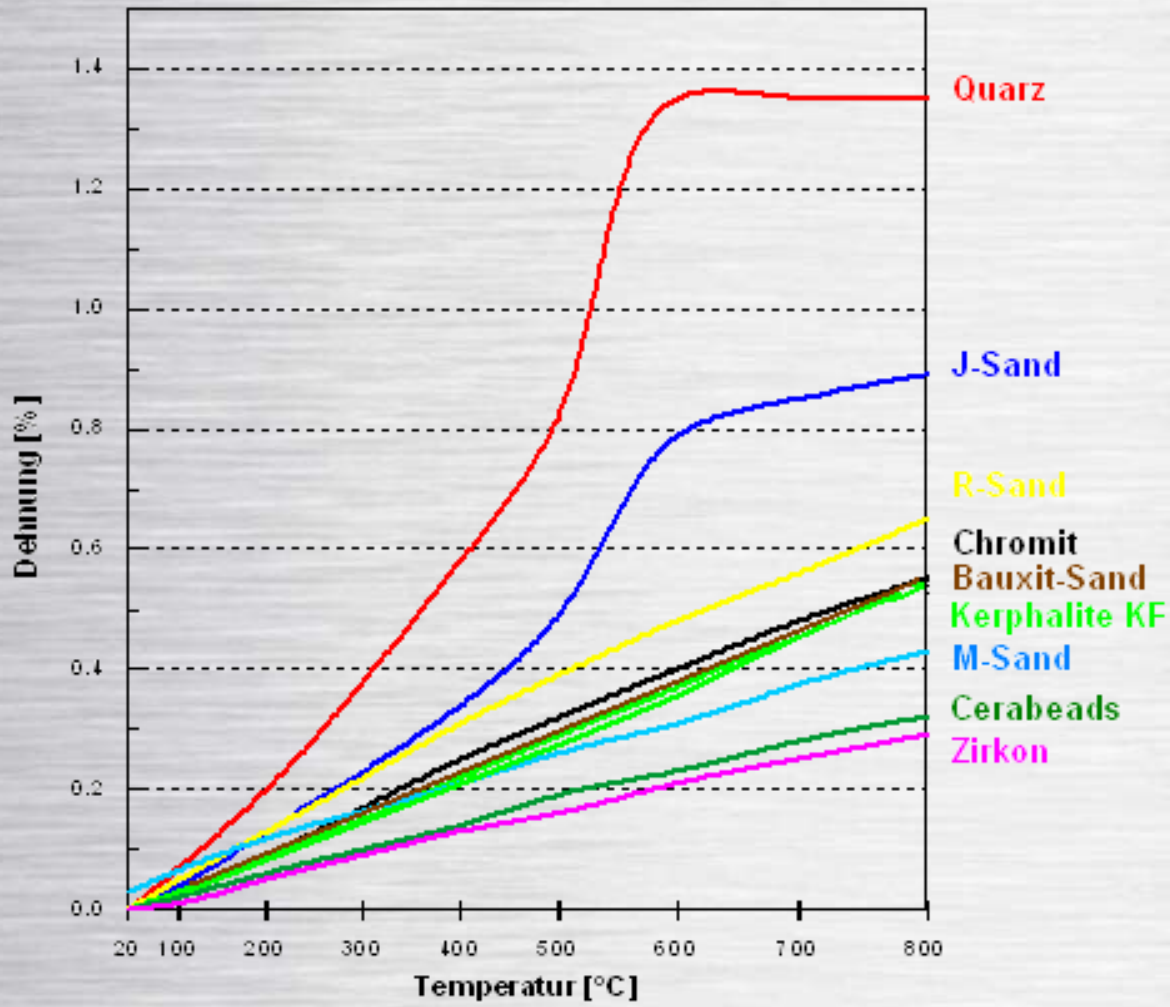
  - All types of substrates can be used. The binder level has to be adjusted accordingly:

1.	Silica Sand	1,0 - 1,8% ☺
2.	Lake Sand	1,3 - 1,8%
3.	Olivine Sand	2,0 - 2,5%
4.	Zircon Sand	0,9 - 1,3%
5.	Chromite Sand	1,0 - 1,5% ☺
6.	Bauxite Sand	1,0 - 1,2% ☺

  - The acid demand has no effect
  - Small amounts of moisture have little effect
  - Best tensiles can be achieved with a round grain silica

2.5. SUBSTRATES AND RECLAMATION (2)

Thermal expansion behaviour of HA´s special sands



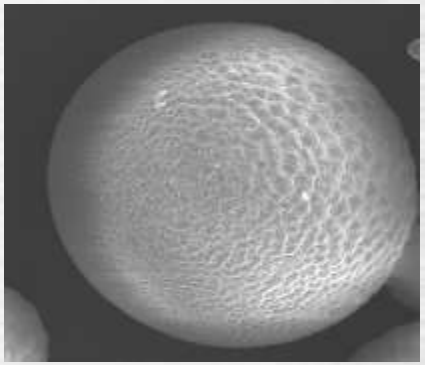
2.5. SUBSTRATES AND RECLAMATION (3)

Bauxite-Sand: One of HA´s special substrates

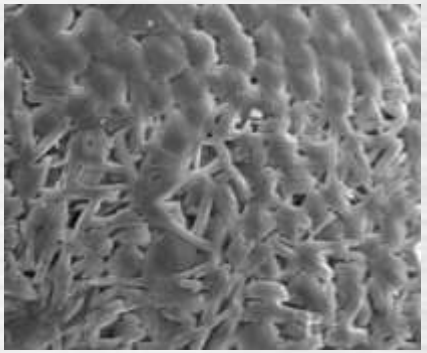
In e.g. Korea, Bauxite sand is one of the prefered substrates for the Sinotherm process

2.5. SUBSTRATES AND RECLAMATION (4)

- Bauxite-Sand
- melting product = molten bauxite
- 75% aluminium oxide + SiO_2, Fe_2O_3, TiO_2
- Specific weight 3.3 g/cm³
- Bulk density 2.0 g/cm³
- Refractoriness SK 36 = 1,780°C
- lin. expansion a 20 - 600°C = 7.2
- fractions AFS 65
- average grain size 0.23 (± 0.02 mm)
- core making with all binders at reduced addition (percent by weight)



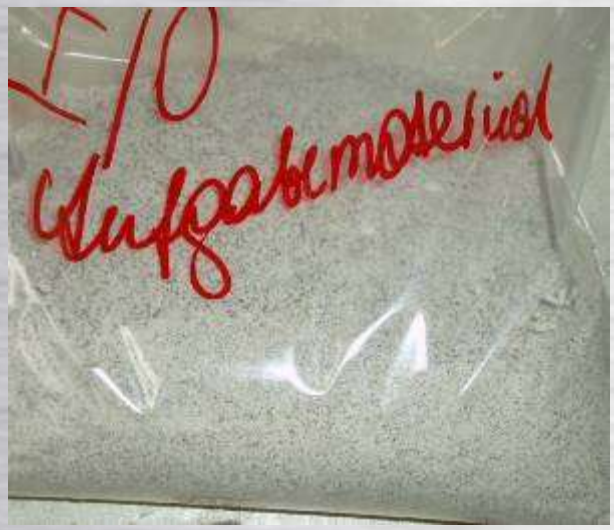
Bauxite sand



Grain surface

2.5. SUBSTRATES AND RECLAMATION (5)

- Bauxite sand does have magnetic properties
- Since a Magnetic separation from silica sand is possible, Bauxite sand is a good alternative for chromite sand



Before separation

After separation

2.5. SUBSTRATES AND RECLAMATION (6)

- **Reclamation**
  - Mechanical reclamation is more common
  - The „Secondary Attrition Process“ is very popular ; LOI target: < 2,0%
  - Reclamation rates of up to 85-90% are possible with a high metal/sand ratio or burn out (Hybrid Resin)
  - Thermal reclamation is less popular and more costly. The sand rebound performance can vary due to remaining salts on the sand grain (conductivity, acid consumption) needs careful monitoring and precautions in use.

2.5. SUBSTRATES AND RECLAMATION (7)

- **Mechanical Reclamation**
  - Alkali Metals can react with the sand surface during casting and change the surface chemistry. Additionally they can remain unreacted in the reclaimed sand making the sand appear “dry” and need extra water addition.
  - Anyhow binder performance and strength will be affected.
  - Consequently a new generation of modified hardeners was developed to
  - increase the strength values on mechanical reclaimed sand and to
  - keep the curing parameters constant at different temperatures
  - A novel part III from HA Germany that will drastically improve the re-usability of reclaimed sand is currently under field evaluation.

2.6. COATING

- **Coatings for Sinotherm**
  - A cured core or mold surface is recommended
  - Water based coatings: Zirkopal or Disopast coatings
  - Solvent based coatings: Zirkofluid coatings
  - Generally some delay after strip is necessary before coating
  - Heat can be applied to accelerate surface hardening. Avoid overheating - secondary cure!
  - Water based coating can be applied to a warm surface; this is not recommended with alcohol based products
  - Water based coatings should be oven dried preferably and alcohol based products can be ignited or air dried.

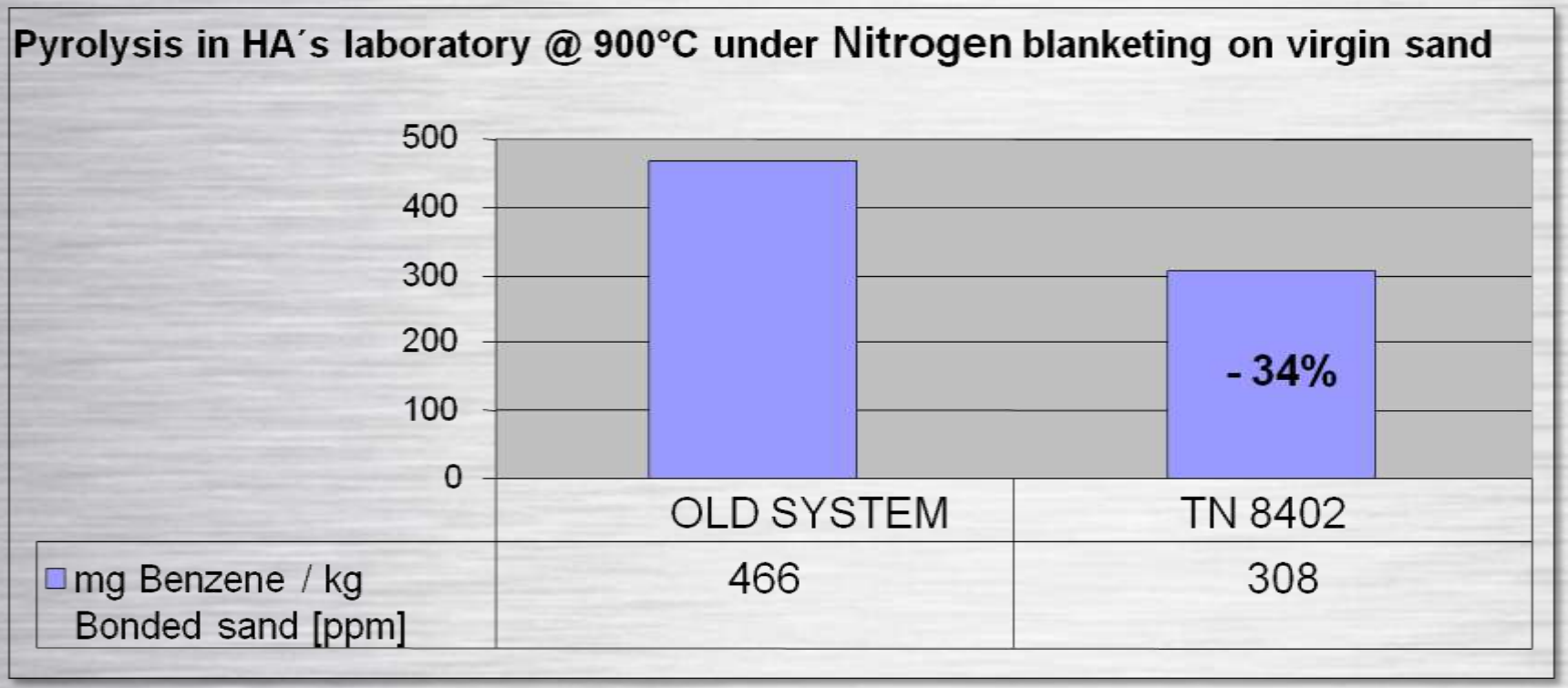
4. Advancements in Sinotherm Systems

- HA working directly in partnership with our customers, has recently introduced a low benzene alkaline phenolic resole resin system, Sinotherm 8402, aimed at reducing benzene emissions on casting.

- The drive to reduce foundry emissions has led to a new technological binder system to improve the environment of the foundry and workplace.

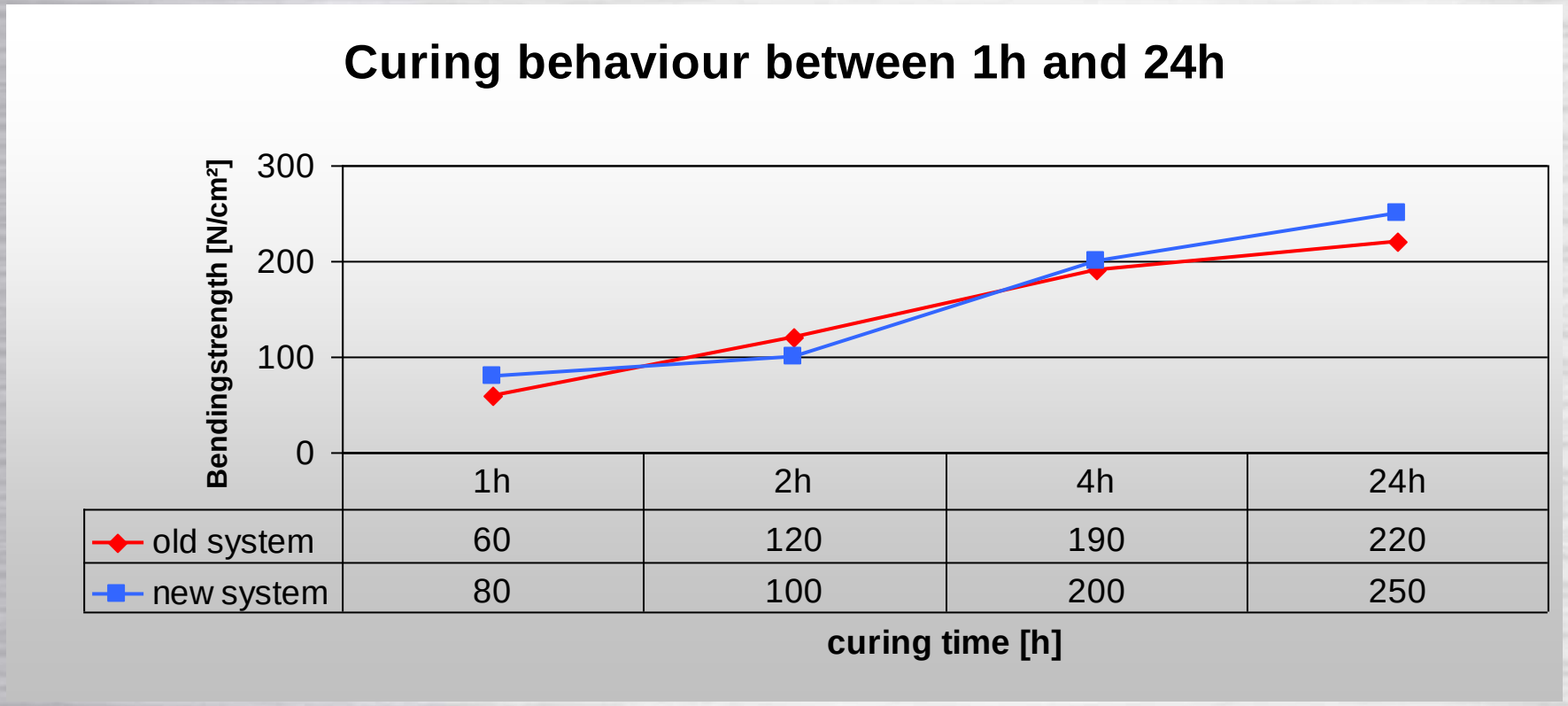
4. Advancements in Sinotherm Systems

- It was found in laboratory experiments that Sinotherm systems produce the maximum amount of benzene emissions - in a temperature range of 700-1100°C – at approx. 900 °C.



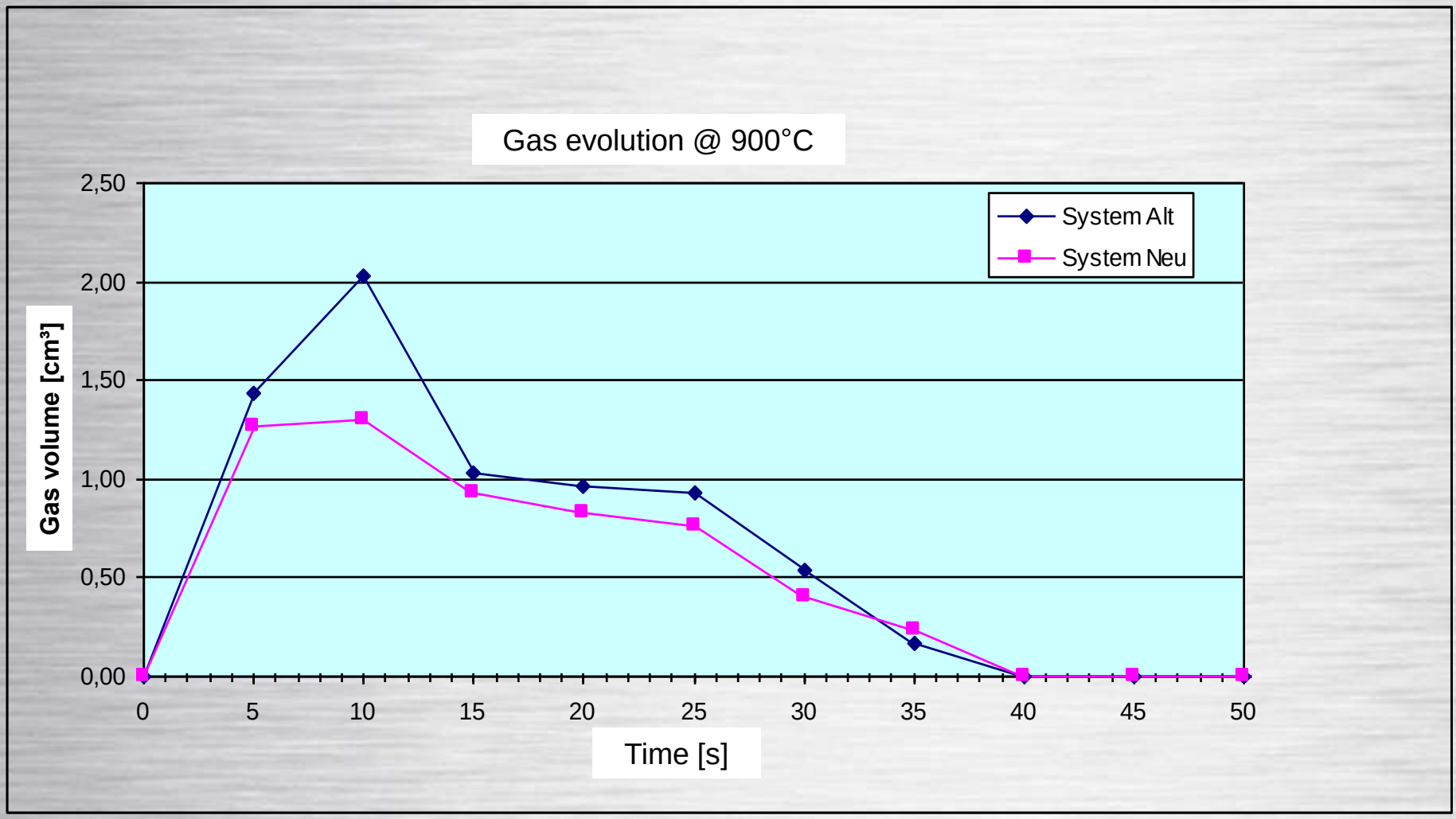
4. Advancements in Sinotherm Systems

Despite the drastic reduction of benzene emissions the curing characteristics could be maintained.
[Old system (blue), TN 8402 (red)]



4. Advancements in Sinotherm Systems

Also the gas evolution generated @ 900°C was reduced

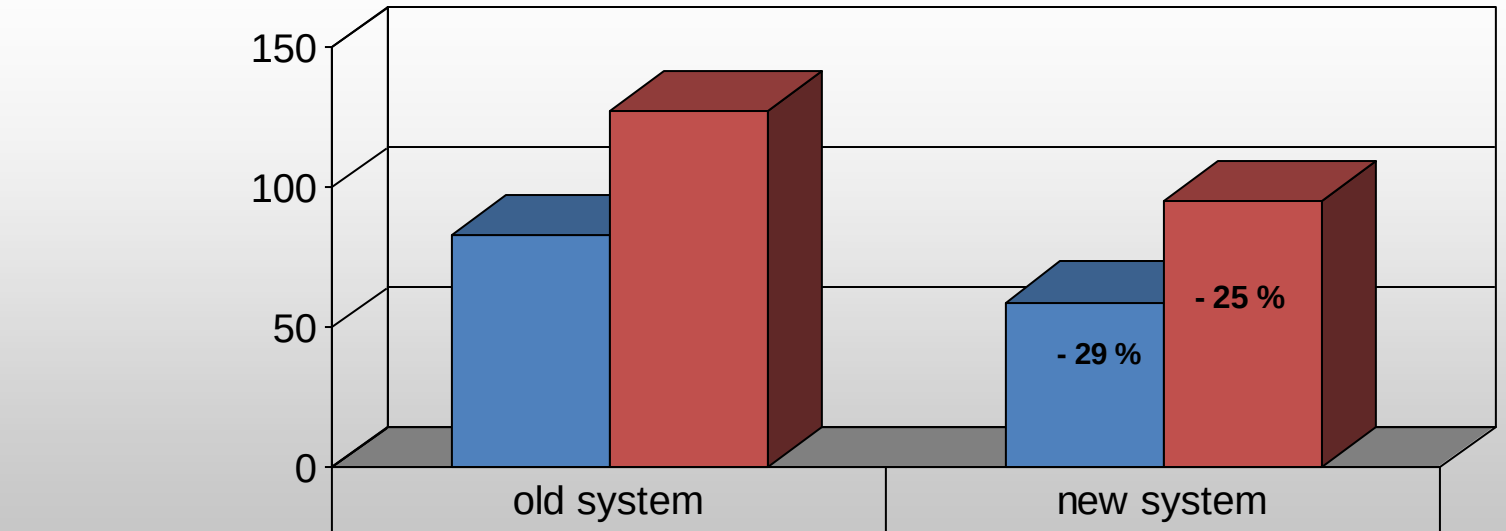


4. Advancements in Sinotherm Systems

In foundry trials (mechanical reclaimed sand) a drastic benzene emission reduction by 29% was confirmed by German authorities

Measurement BGIA

(Standard process 6265)



	old system	new system
ppm benzene	83	59
ppm aromatics	127	95

4. Conclusion

- ECP resin technology has been available for approaching 30 years. Hüttenes-Albertus recognises the challenges facing ECP's in the future and is continually improving resin & ester's inline with foundry production requirements, cost drivers, environmental legislation and advancement in casting process technologies.

5. Conclusions and Discussion