«Up To Date Experience With Treated Leonardite and Its Benefits On Green Sand Molding»

«Yaş Kalıplama Tekniğinde Leonardit Kullanımı ve Avantajları»

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4.Oturum: Kalıp ve Maça Teknolojileri

4th Session: Mould&Core Technologies

Oturum Başkanı/Session Chairman: Dr. Türsen Demir (Çukurova Kimya End. A.Ş.)

up-to-date experience with treated Leonardite and its benefits on Green Sand Moulding

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Introduction

- In order to remain a widely used, modern and efficient molding technology throughout the world, the green sand process must continuously evolve by the application of technical and environmental improvements.

- Many years of experience demonstrate that appropriate additions of **leonardite to blends of bentonite can address environmental issues while providing excellent technical performance benefits**.

Introduction

- The presentation outlines a review of the anticipated changes to sand properties and the associated expected benefits.
- Although there are a number of factors impacting sand systems, experience has given us indications of the most likely changes that we can expect when adding different proportions of **leonardite** and bentonite to green sand. We have developed a list of sand properties and the likely degree to which **leonardite** will impact them in your sand system.

Treated Leonardite (FloCarb ®)

- **Leonardite** is a carbonaceous additive to enhance quality, improve performance, and provide stability for foundry green sand systems.
- AMCOL have developed Leonardite as a proprietary material produced at their plant in Gascoyne North Dakota, USA.
- Before we explore Leonardite in green sand we will first explain the origins of this material.

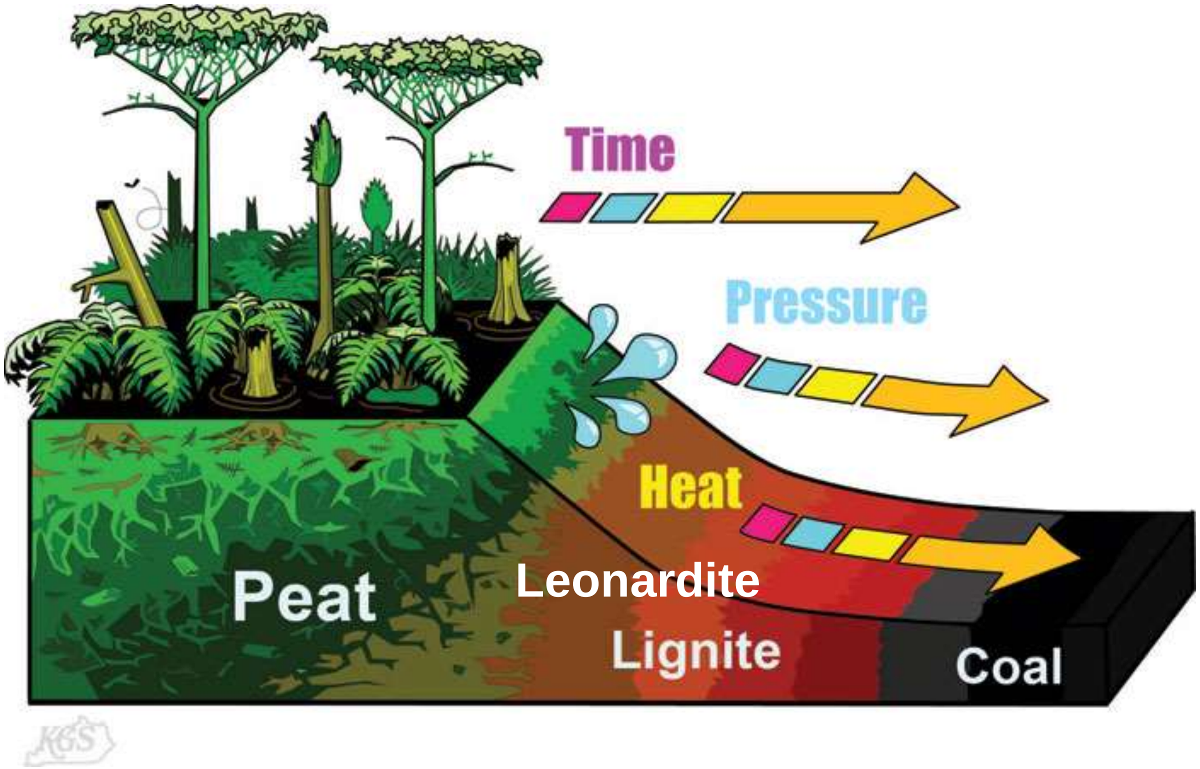
- This deposit was discovered by Dr Leonard, hence the name given to the mineral (leonardite).

- Highest grade in North America is mined from North Dakota

A. G. Leonard on horseback in North Dakota circa 1910

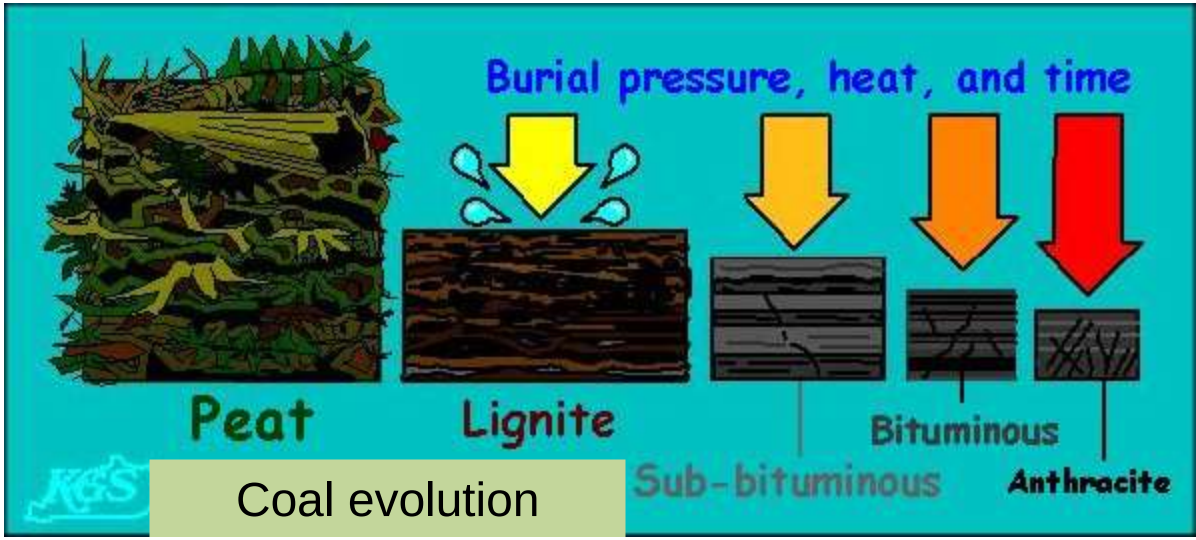
- Predominantly made of complex, naturally occurring organic acid(s)
- Highly oxidized form of organic matter

Formation of Coals



What is coal dust (or seacoal)?

– Typically, seacoal is a “highly volatile bituminous coal” ground to a specific size and having following main characteristics:
  - 34 - 39 % Volatiles (VCM)
  - 3 - 9 % Ash



Coal evolution

a low rank coal.

Peat

Leonardite

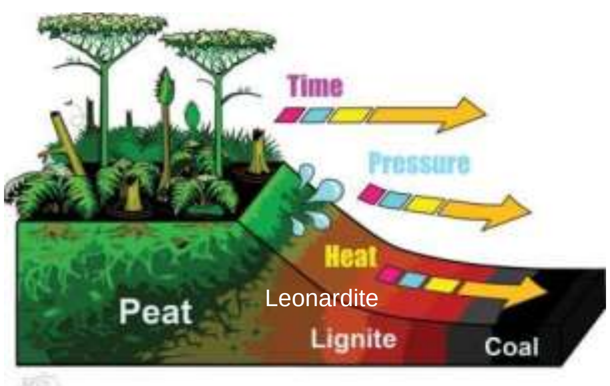
Lignite – Brown coal

Sub-bituminous

Bituminous – typical foundry coal

Anthracite

- As age increases
- Coal rank increases
- Carbon content increases
- Oxygen Content decreases
- Chemical reactivity decreases
- Hardness increases
- Volatile organic matter decreases



AMCOL owns and mines Leonardite for three main market applications

Agriculture

Plant Growth Enhancer
pH 4

Foundry

AMCOL METALCASTING

Green sand enhancer
pH 7

Oil Drilling

Drilling mud viscosity reducer
pH 4 & 9

How does **Leonardite** enhance green sand systems

- Firstly we need to understand how Bentonite and water form a binder to hold sand grains together
- There are basically two types of Bentonite
  - **Sodium montmorillonite** – sodium aluminium silicate

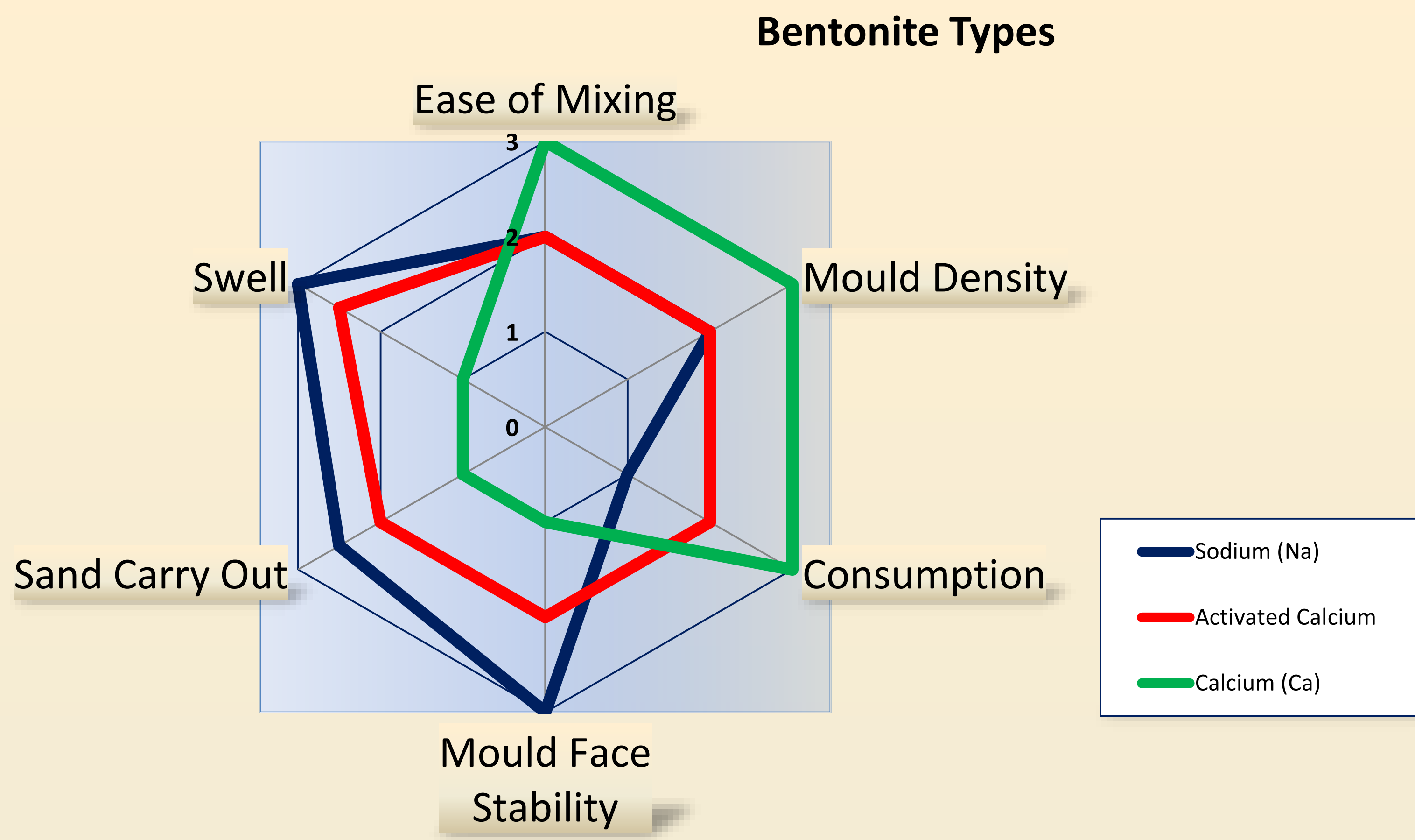
    Sodium is the primary exchangeable ion, but there are others present
  - **Calcium montmorillonite** – calcium aluminium silicate

    Calcium is the primary exchangeable ion, but there others are present

  Also commonly used are **Activated Calcium Bentonite**

    These are Calcium Bentonite treated with a Sodium material that replaces most of the Calcium ions with sodium ions

Bentonite Types – property comparison



Bentonite Types

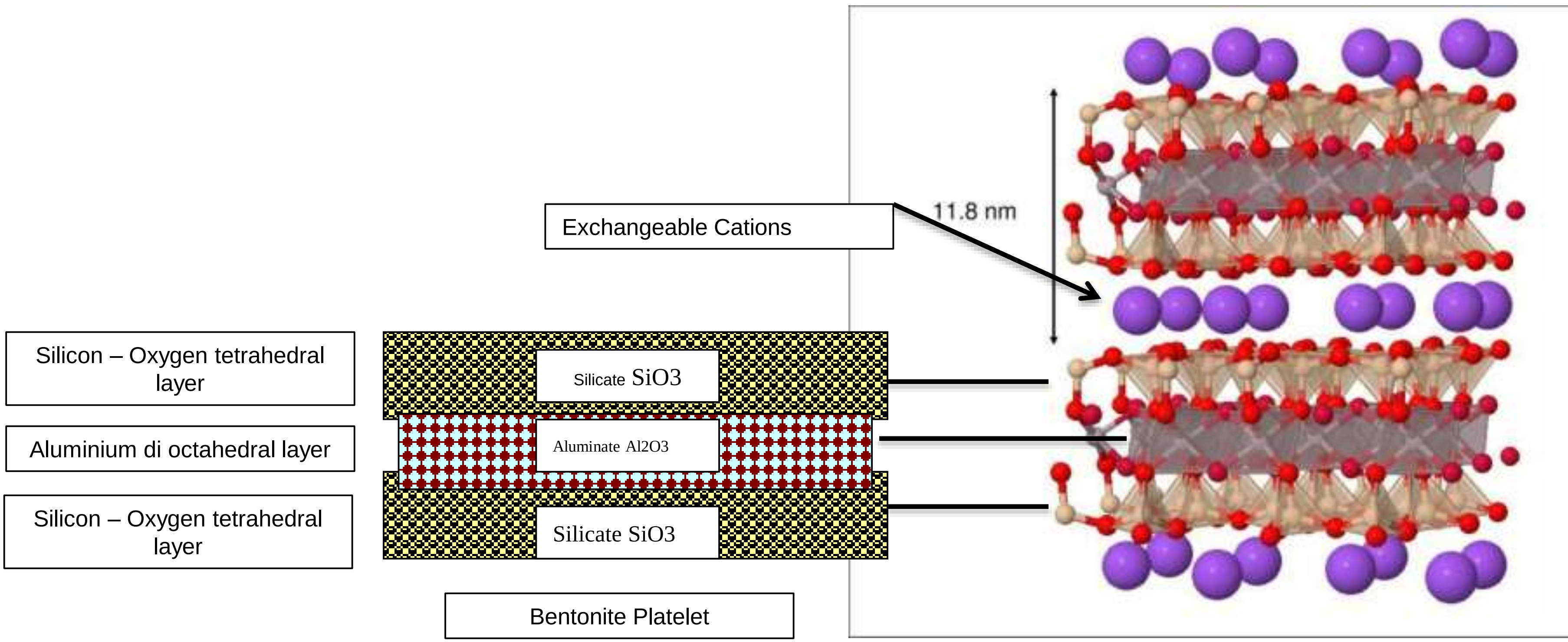
Sodium Bentonite	Calcium Bentonite
• Higher thermal durability • High viscosity – high swelling • Difficult to mix • High tensile strength • High WTS • Good moisture retention • High hot and dry strength • Difficult shakeout • Lower GCS	• Lower thermal durability • Lower viscosity – lower swelling • Easy to mix – strength development • High GCS • Good flowabilty • Lower hot and dry strengths • Easy shakeout

Bentonite Structure – Sodium Bentonite

Bentonite has a complex, microscopic structure

1 Bentonite platelet is 11.8 nm

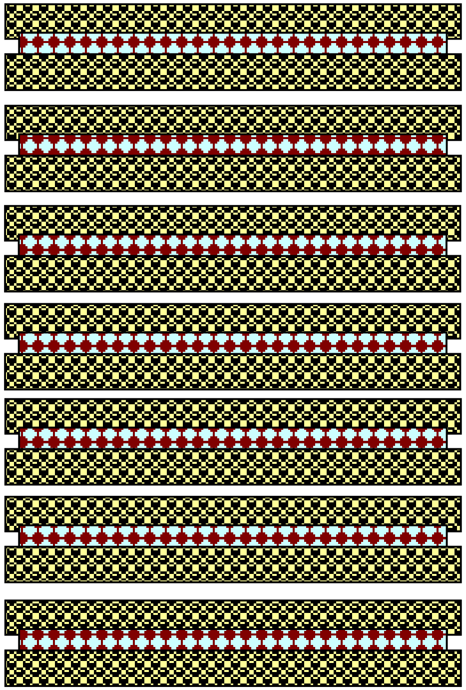
nm = nanometre or 1 billionth of a metre

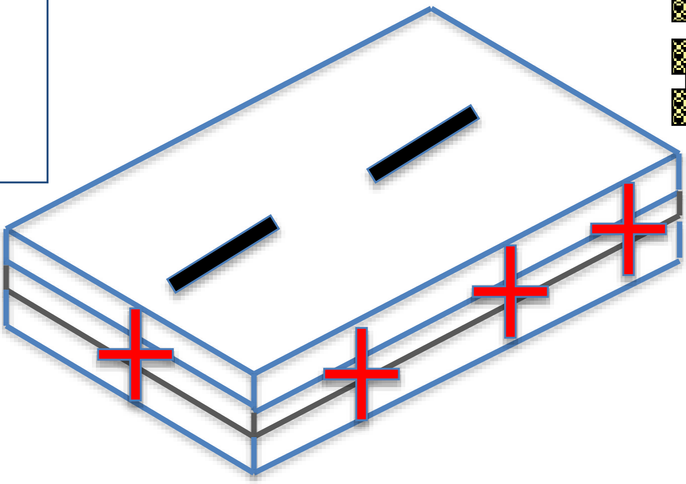


Dry Bentonite

•Dry Bentonite is structured as a stack of microscopic platelets similar to a deck of plating cards.

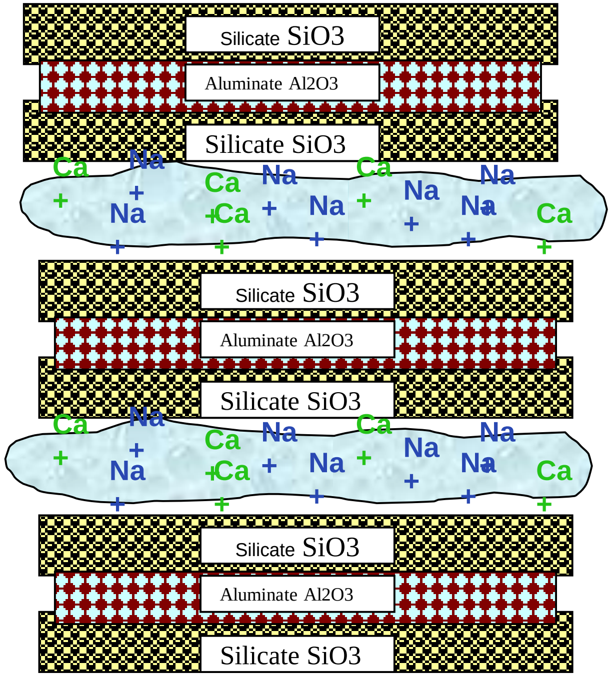
•Each Platelet has a positive charge on its edges and a negative charge on its flat surface





Water and Bentonite

- As water is added to the Bentonite, the water molecules link up between the platelets causing the negative charges on the surface of the platelets to become more pronounced (increase)
- As this charge builds up, the platelets start to pop apart and the Bentonite starts to swell.

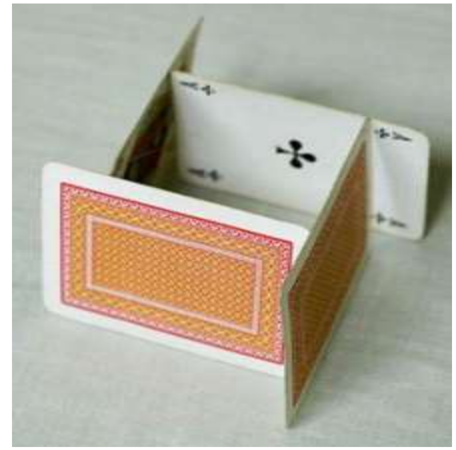


Bentonite Swelling

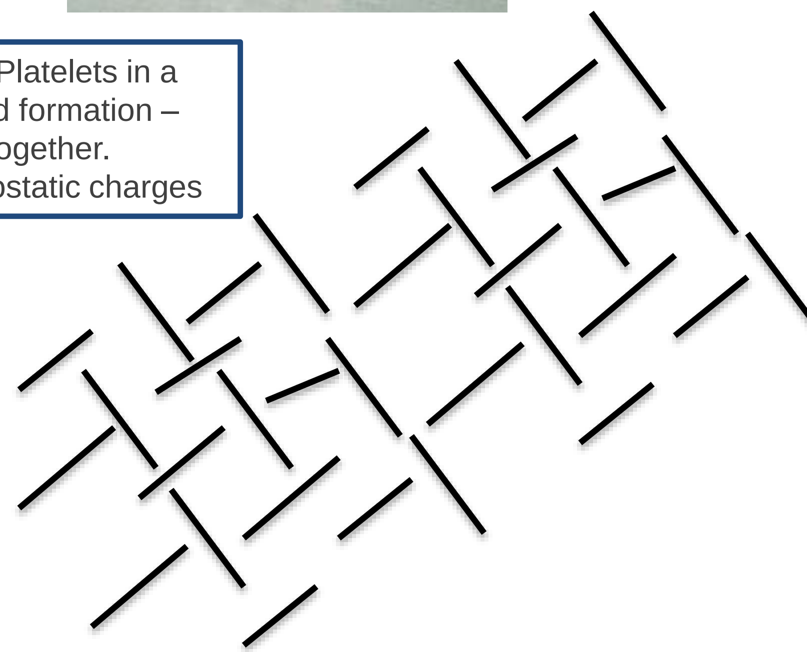
- Bentonite has a fundamental property to adsorb water and expand.
- The level of absorption and swelling depends on the type of exchangeable ions contained.
- Swelling is mainly due to 2 factors
  - Water absorption @ platelet surface level
  - Osmotic repulsive forces
- Sodium (Na+) allows water to penetrate thru the platelets forcing them apart
- Calcium (Ca++) is hydrated the same way, but due to its strong + charge has lower absorption properties not permitting as much water to penetrate the platelets

House of Cards

- As additional water is added, it is attracted to the negative charged faces and crowds in between the dispersed platelets where it is held in place by the electrical charges.
- As the water continues to be added and the platelets continue to gain mobility, the platelets arrange themselves, positive edge to negative surfaces until they have completely arranged themselves into a microscopic "House of Cards" formation.

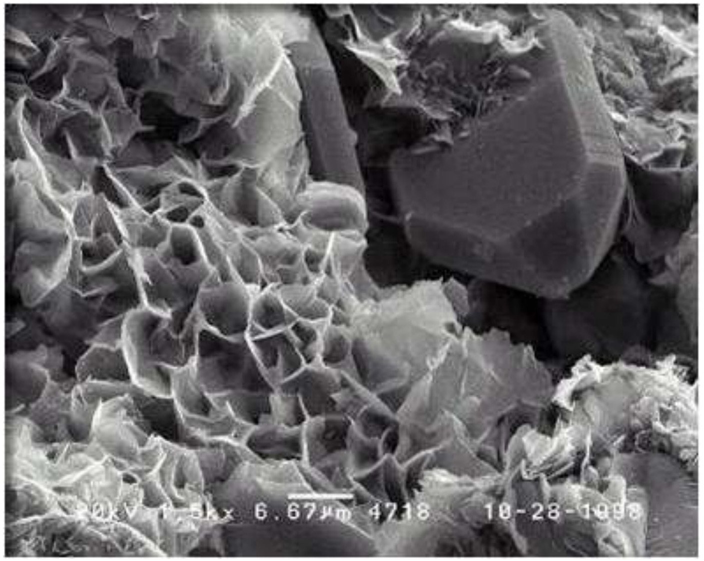


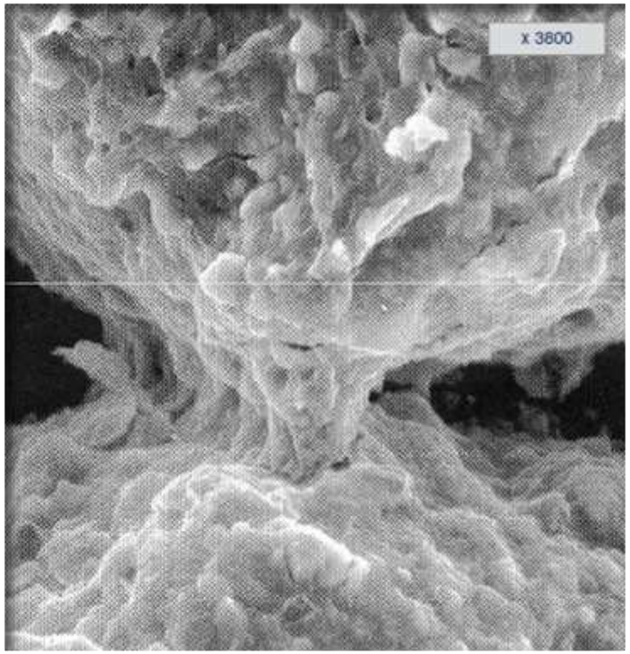
Microscopic Platelets in a house of card formation – gelling together.
Held by electrostatic charges



SEM Showing House of card structure

Bentonite bridge between sand grains

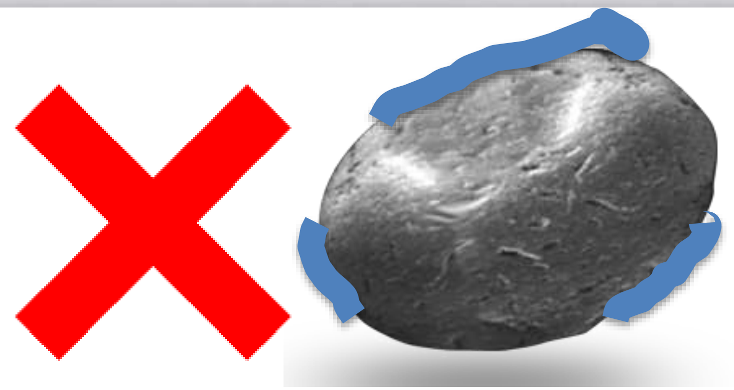




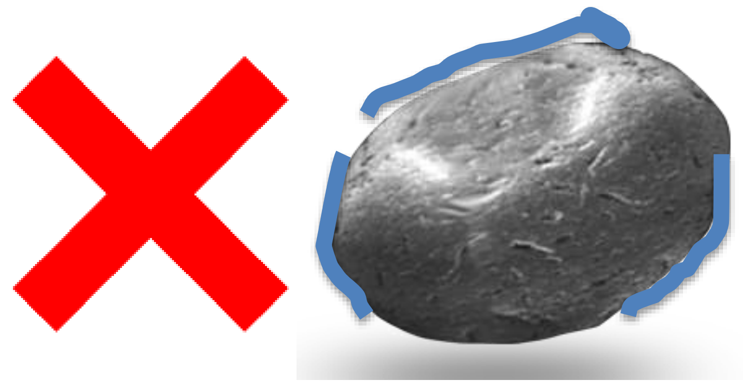
Binder dispersion

- In order to maximise the advantage of electrochemical bonding, and provide a thin uniform coating of the sand grains, the binder (Bentonite & Water) must
- Uniformly mixed
- Evenly distributed throughout the green sand system

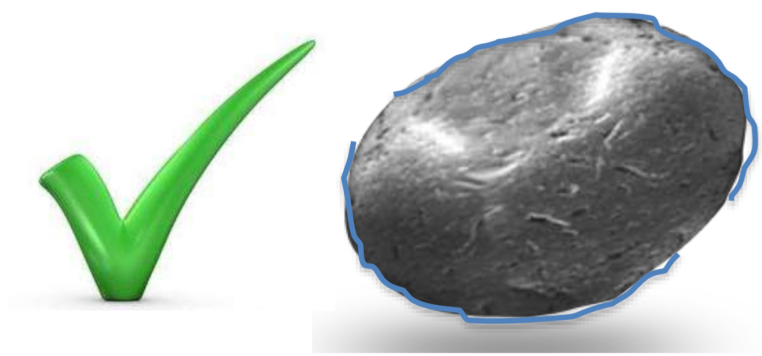
- The more uniform the coating on the sand grains, the better the quality of the green sand



Thick, poorly distributed clay layer



Improved, but still poorly distributed



Thin even coating of the sand grains

Mulling / Mixing Process

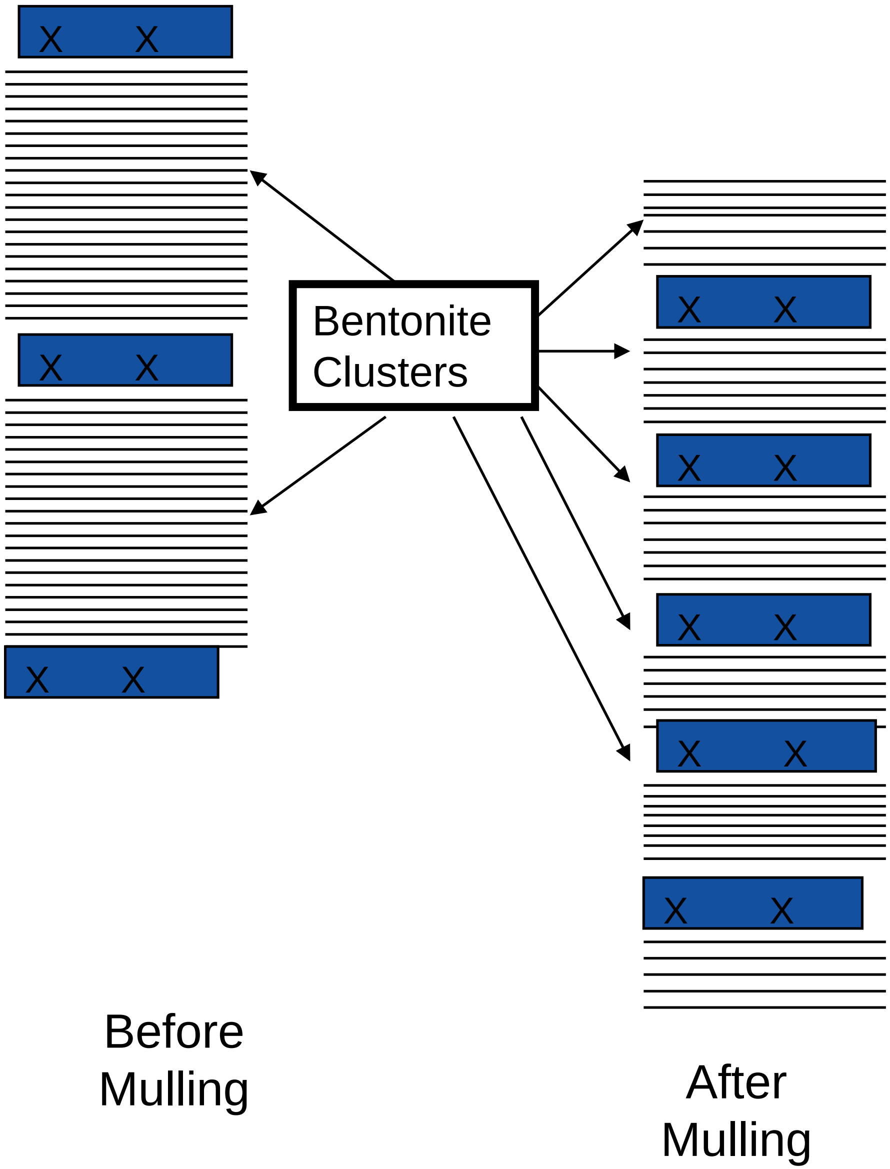
•The mulling / mixing process must be complete enough so that the water is evenly distributed throughout the Bentonite mass.

•It must be able to get to the smallest groupings of Bentonite platelets.

•The mulling / mixing must shear the Bentonite platelets apart exposing the flat surfaces to the moisture.

•Failure to achieve this results in Bentonite not being fully hydrated and free moisture being present.

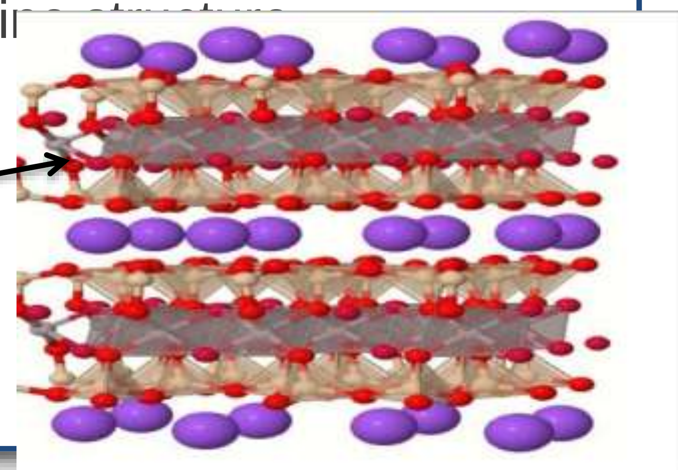
•The free moisture is not combined with the Bentonite, it is surrounding it, this is a major cause of casting rejects.



Bentonite and water association

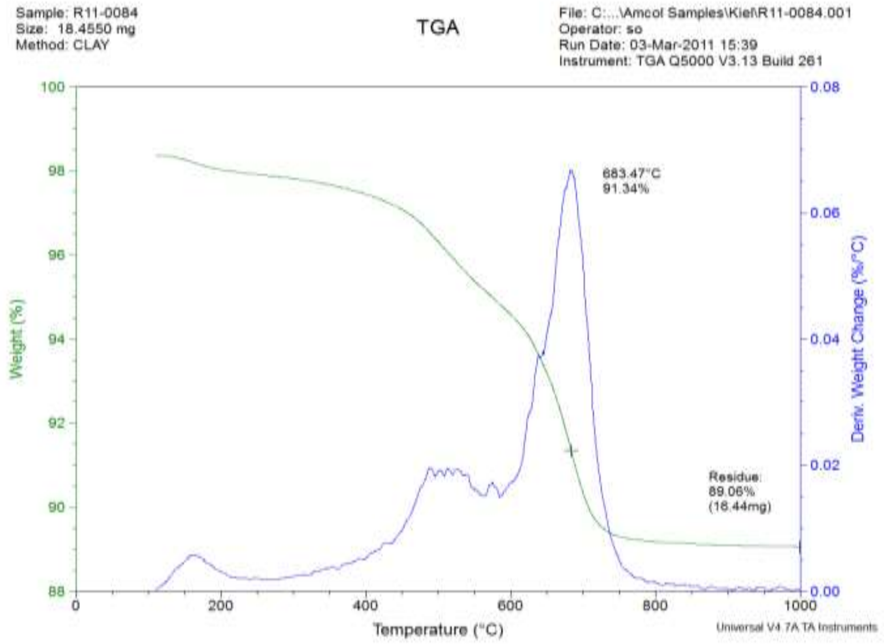
- Bentonite compounds are fragile both chemically and structurally
- The composition of Bentonite contains water and exchangeable ions as in integral part of the mineral structure
- **Water is associated with Bentonite in two types**
  - **Water that is an internal part of the crystal structure (crystalline moisture)**
  - **Water that is absorbed between the platelets.**
- The Crystalline moisture is an integral part of the mineral and cannot be removed without destroying the crystalli

Crystalline water held in the Bentonite structure



Bentonite and water association

- At low temperatures (mulling / mixing) Bentonite will absorb moisture (due to ionic bonding) and undergo ion exchange with the temper water.
- At higher temperatures, the Bentonite will loose its absorbed moisture thru evaporation
- And at higher temperatures **it will loose its crystalline moisture and be damaged** / destroyed rendering it useless as a binder material



Green Sand Recycle

- The Bentonite directly adjacent to the casting is completely destroyed (sintered).

- Some of the remaining Bentonite in the green sand system experiences varying degrees of thermal damage to its crystalline structure.

- The extent of the damage to the crystalline structure determines the degree to which the Bentonite can reabsorb temper water and regain the plasticity and electrochemical bonding characteristics to be a good binder.

Green Sand Recycle

- Since most of the green sand is recycled, there is a high degree of Bentonite that has experienced some degree of **thermal exposure and structural damage.**
- Also as the green sand is recycled, the hard water minerals from the temper water get exchanged for the sodium and potassium ions in the Bentonite.
- **Over time, this decreases the Bentonite ion exchange capabilities and makes it more difficult to reabsorb moisture**

Summary – what we know so far

- Bentonite platelets are microscopic, and contain + and – charges
- When water is introduced, an ionic bond is formed, and the platelets arrange themselves in a formation known as House of cards
- This formation exist when the Bentonite slurry gels
- Bentonite and water must be distributed evenly throughout the green sand to achieve a thin, uniform coating of the sand grains.

Summary – what we know so far

- The mulling / mixing must shear the platelets apart to expose the surfaces to the water.
- Bentonite crystalline structure contains internal moisture.
- When this is lost thru high temperature damage, the Bentonite is longer useful as a binder.
- Continued cycling of green sand leads to loss of ion exchange capacity thru thermal damage and minerals contained in temper water – making it more difficult for Bentonite to reabsorb moisture.

How can Na Bentonite be improved?

- As Na Bentonites are most widely used in ferrous greensand applications, there is a need to overcome some of the inherent difficulties with these Bentonites
- Namely, **ease of mixing, strength development, sand flowabilty, reduced permeability and difficult shakeout**
- These are often overcome by blending Na and Ca clays together. This is sometimes detrimental to the durability and hot strength of the system, depending on the type of castings and sand:metal ratio being used.

How can Na Bentonite be improved?

- There is also need to try and **reduce the quantity of Bentonite consumed**, which is partly due to the varying degrees of thermal damage to the crystalline structure of the Bentonite, which needs to be replaced with more new Bentonite.

- It is for the reasons above that AMCOL have developed a material which reduces these difficulties

To improve Na Bentonite

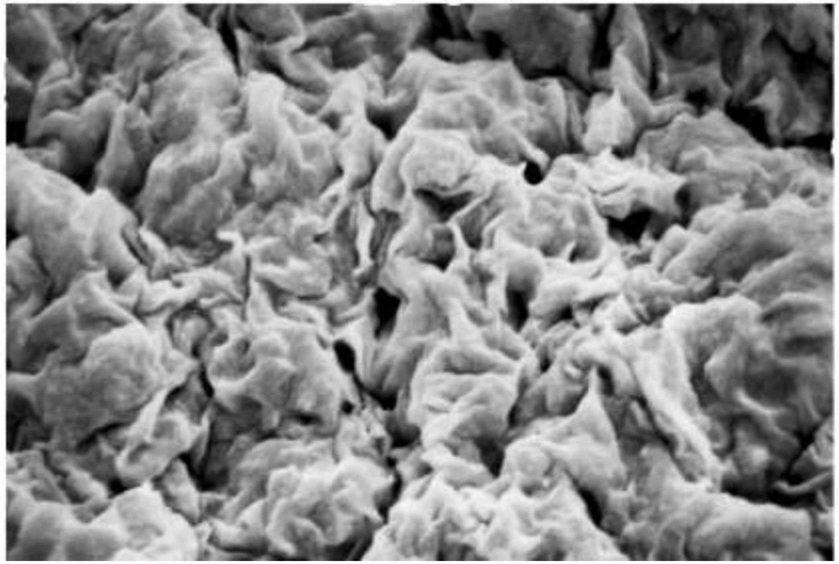
- Reduce clay viscosity
- Improve flowabilty
- Improve muller efficiency
- Increase mold permeability
- Maintain water absorption and retention
- Improve shakeout
- Improve foundry environment
- **Maintain Thermal durability**

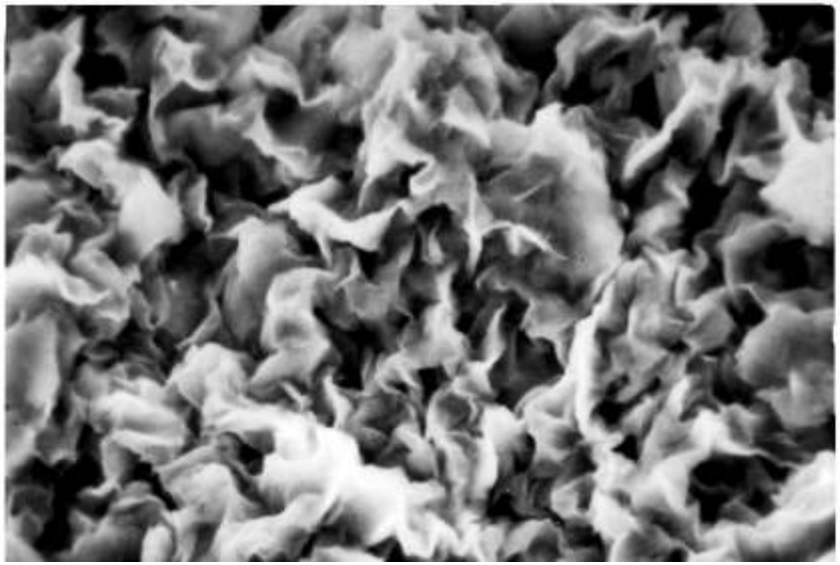
Treated lignite (FloCarb ®)

- It is **not** a wetting agent
- It has a high CEC and functions at a molecular level
- It alters the clay platelet bonding in reducing the inter – particle forces that hold the platelets together
- This reduces viscosity and increases moisture retention

The reduction in the clay inter-particle forces is readily observed as an increase in the clay surface area available for hydration, with a subsequent increase in clay particle dispersion and moisture retention

Hydrated Sodium Bentonite – Tightly bound	Treated Leonardite – Open and porous





Typical **treated Leonardite** Properties compared to Seacoal

Material	pH	VCM %@ 982˚C	Fixed Carbon %	Ash %
Seacoal	7	34 – 40	50 – 60	10% Max
Treated leonardite	6 – 8	45	45	15%

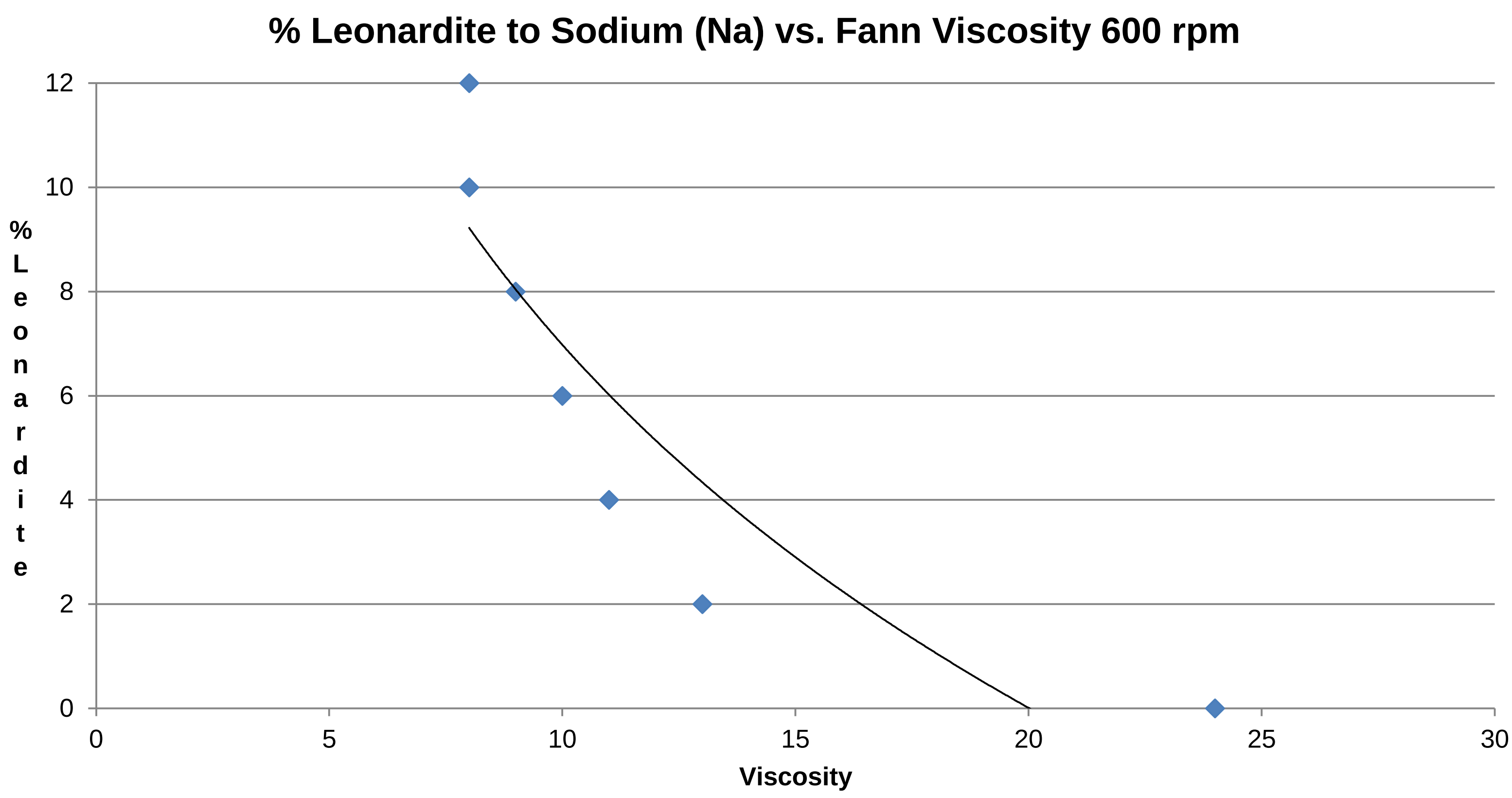
How does **Leonardite** work ?

- Treated Leonardite works **in two important ways to recondition the Bentonite to regain the plasticity and electrochemical bonding characteristics necessary in a good binder.**
- Nothing can be done for the burned-out Bentonite, it must be purged from the system so new Bentonite can be added to keep the system stable.
- For the partially damaged Bentonite platelets, repeated cycles with Leonardite will work to improve their structure and make them more electrically active with improved electrochemical bonding characteristics.

How does Leonardite work ?

- Continued treatment with Leonardite will also regenerate the exchangeable ions in the crystalline structure which improves the ability to absorb moisture.
- This improvement results in a higher CEC, which is reflected in a higher MB Clay level.
- This allows for a lower addition of clay to achieve the same or better properties

Treated Leonardite Reduces Clay Viscosity



Treated Leonardite – Influence on system sand properties with pouring cycles

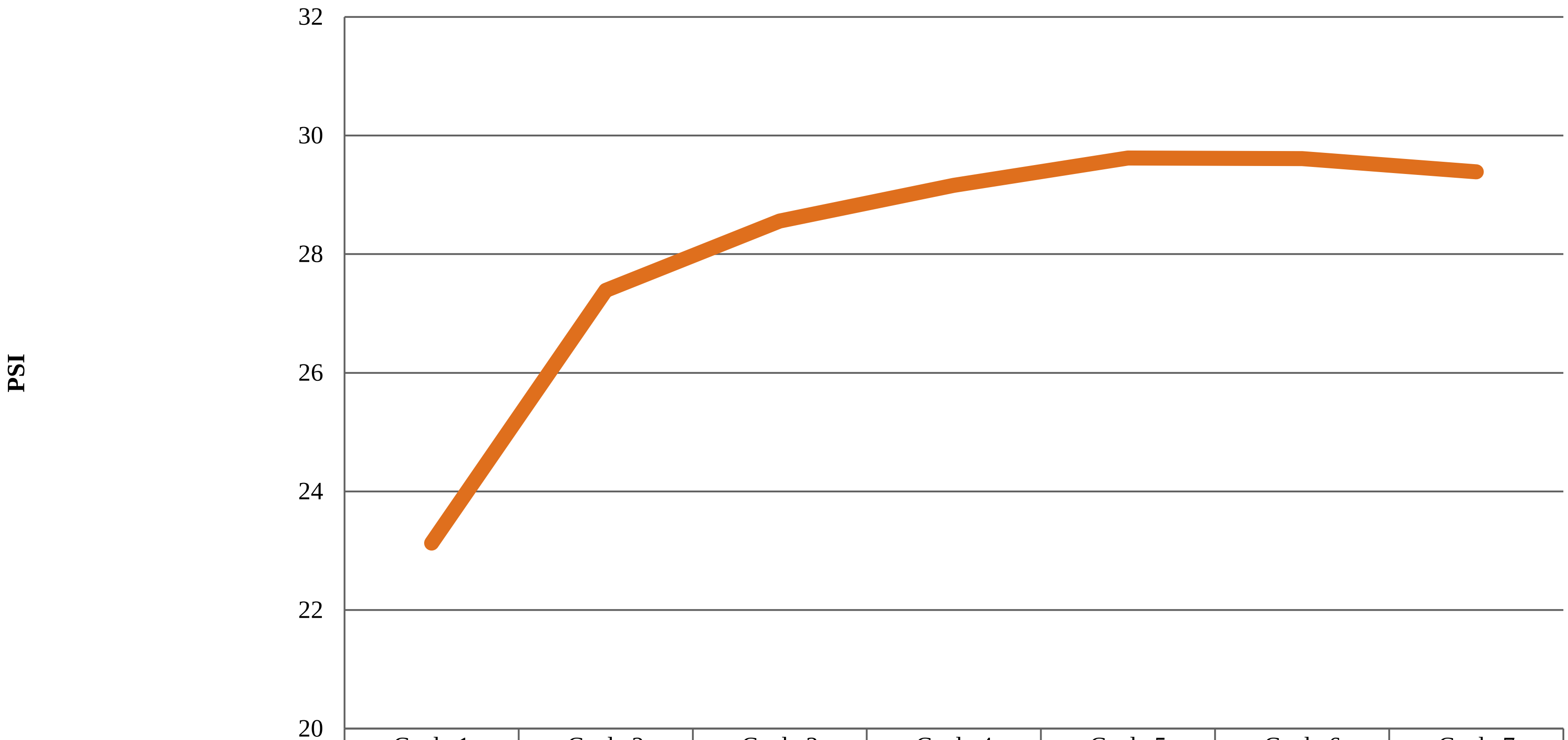
- The effect of leonardite within a sand system, takes some time to impact on the Bentonite properties.
- It is therefore difficult to duplicate the normal foundry results within a single laboratory test.
- AMCOL, together with the University of Northern Iowa Metal Casting Laboratory conducted a test to simulate a foundry operation.

Treated Leonardite – Influence on system sand properties with pouring cycles

- The experiment design was as follows
  - Simpson 500 Kg Muller – mixing time 7 to 10 min
  - Silica Sand (Wedron 520)
  - 8% Sodium Bentonite
  - Carbonaceous additives – 20% of dry Bentonite weight
    - Seacoal – 10% of Bentonite
    - Leonardite – 10% of Bentonite
  - Herman High Pressure Moulding machine – B Scale Hardness 92 – 95
  - Compactability target 39
  - 7 Complete casting cycles - maintaining Clay, CB and combustible materials. 3 moulds poured for each cycle

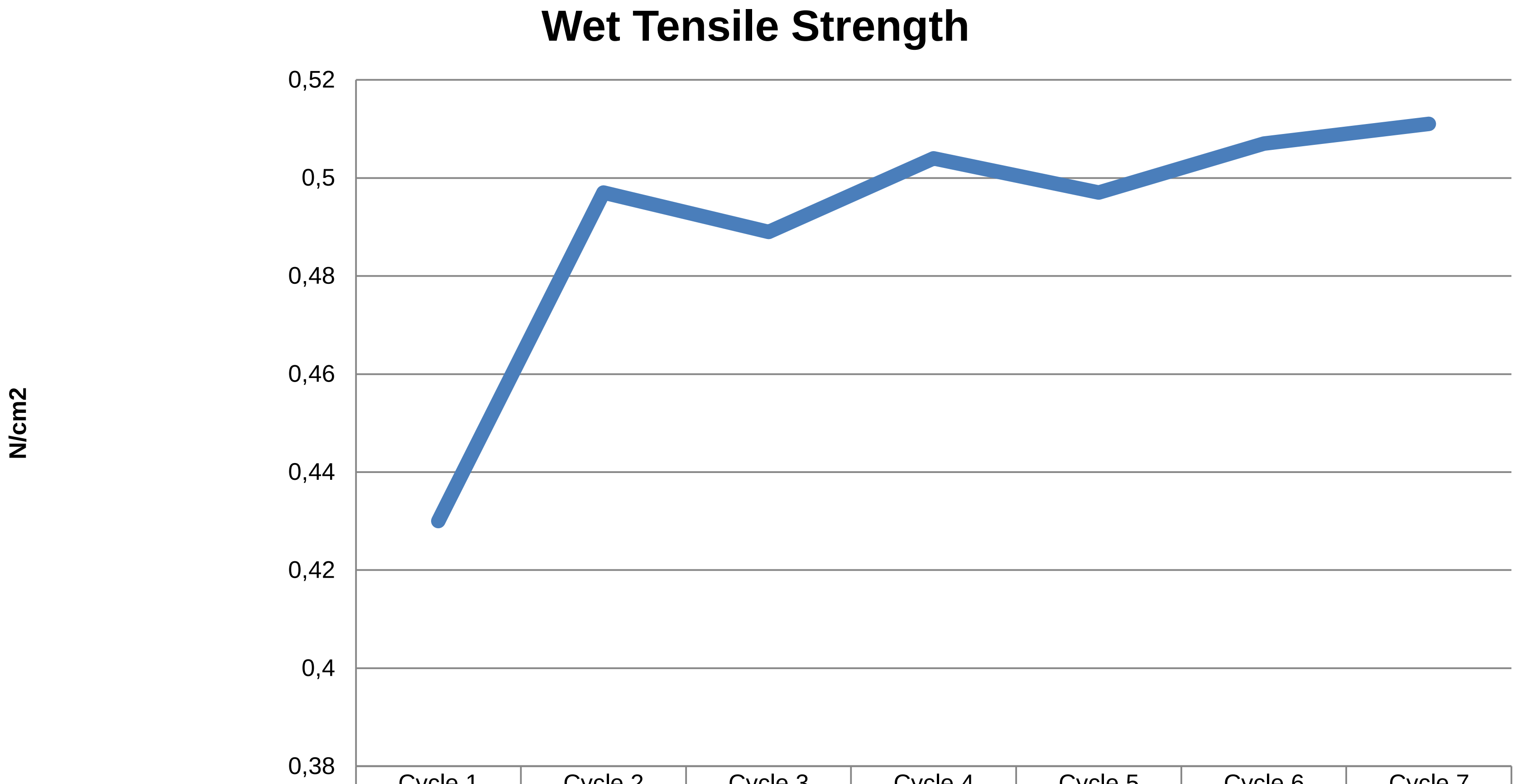
GCS increases after one cycle, indicating the Leonardite impacting on the Bentonite properties

Green Compressive Strength



	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7
FloCarb 10% of Bentonite	23,13	27,39	28,56	29,16	29,62	29,61	29,39

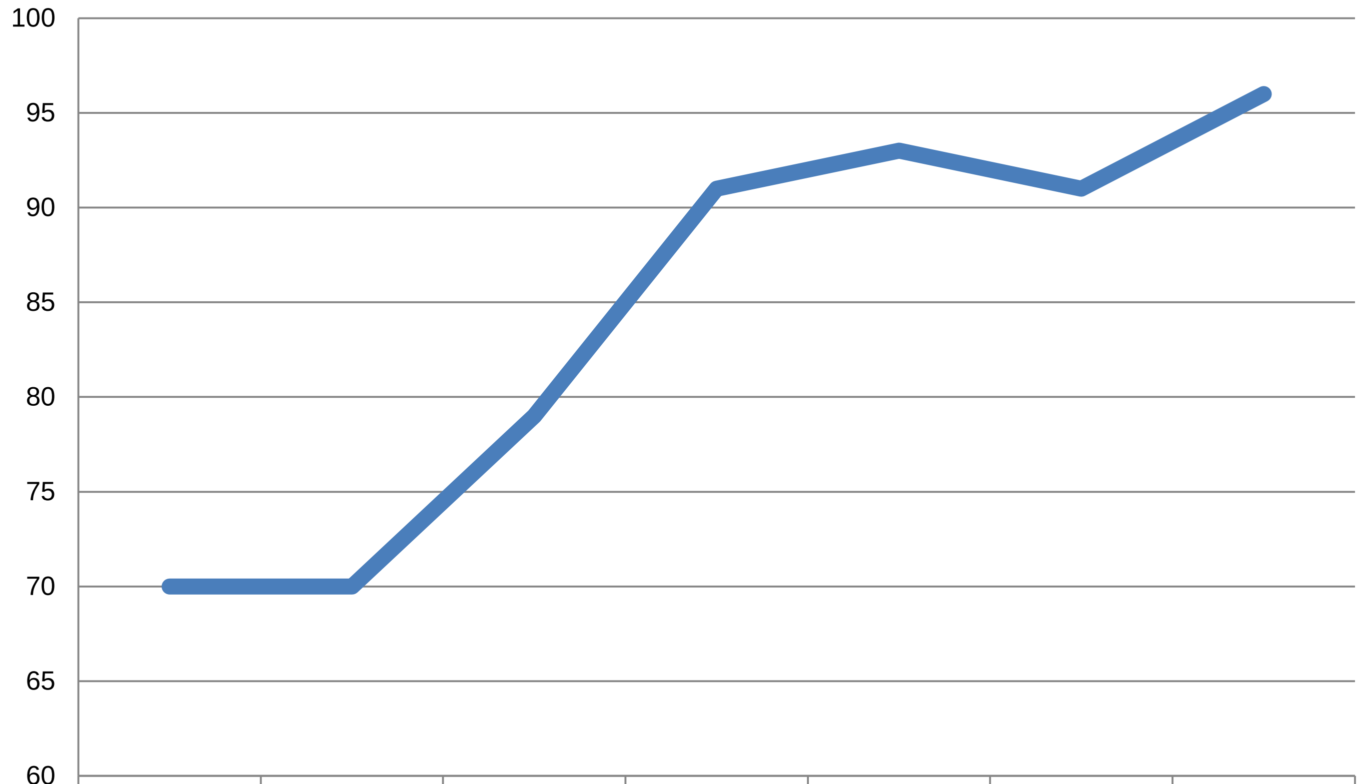
WTS shows a similar trend to GCS – reflecting the Leonardite impacting on the Bentonite



	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7
FloCarb 10% of Bentonite	0,43	0,497	0,489	0,504	0,497	0,507	0,511

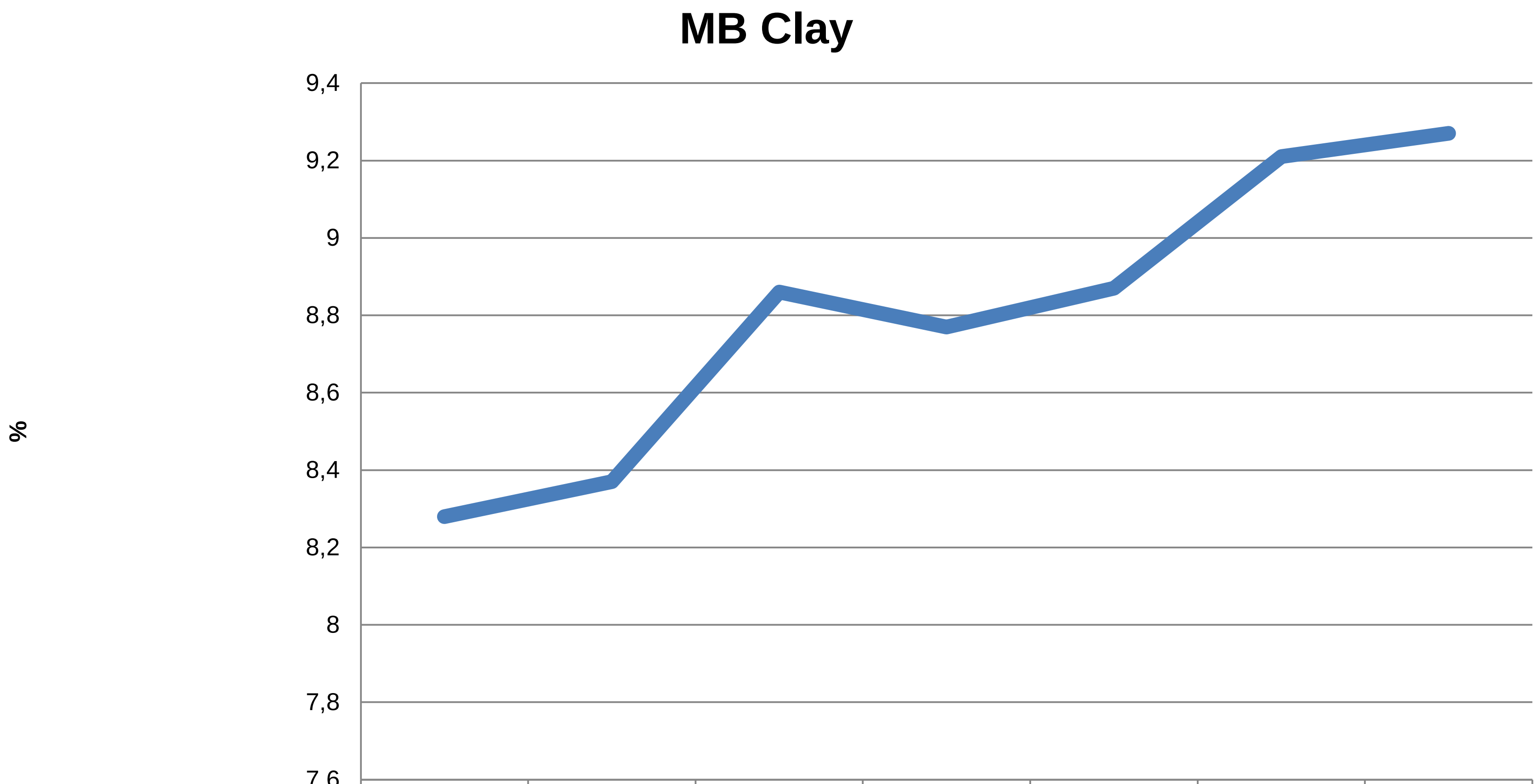
Permeability increases with progressive cycles

Permeability



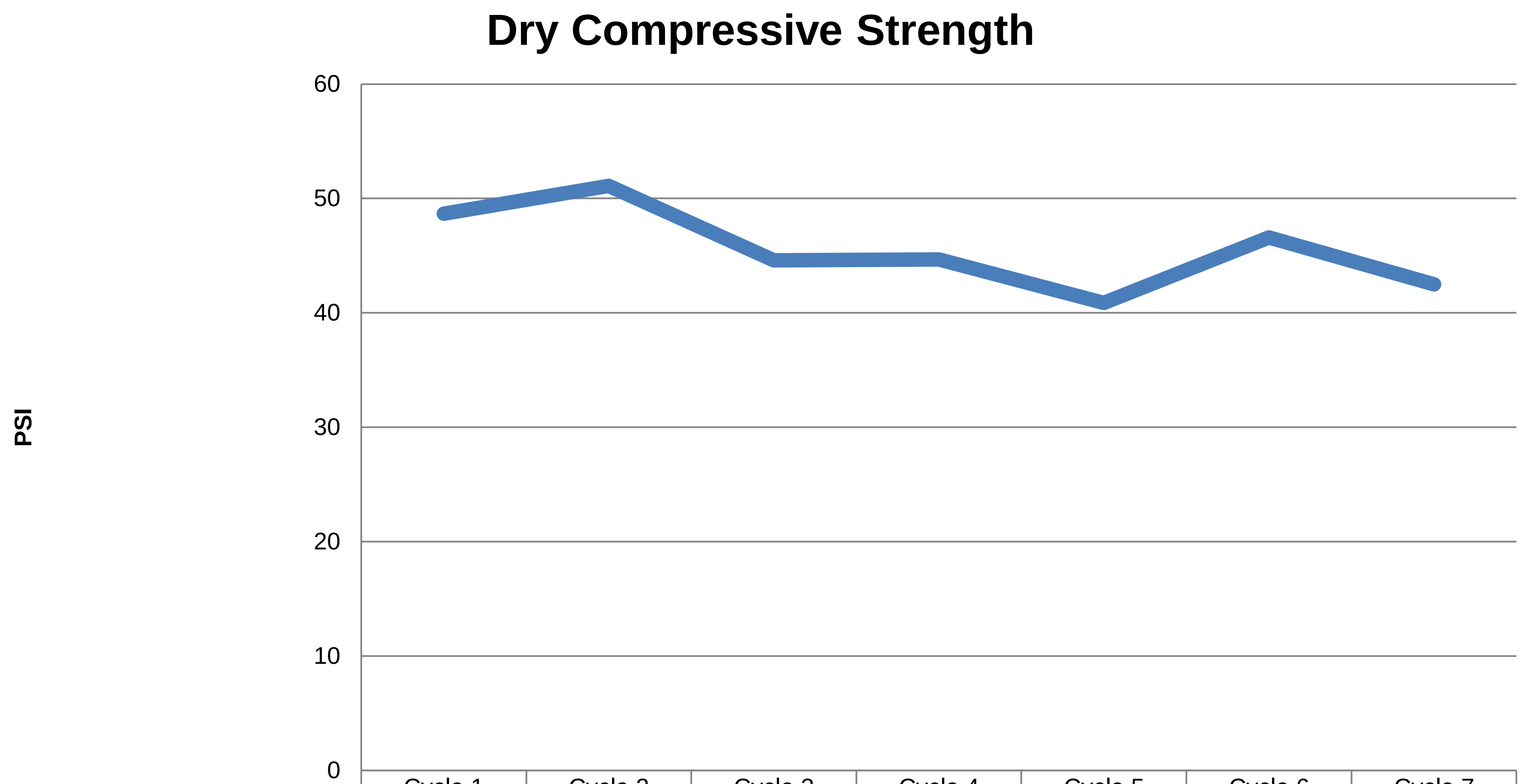
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7
FloCarb 10% of Bentonite	70	70	79	91	93	91	96

MB Clay Increases for the same level of Bentonite in the sand – the clay becomes more active with Leonardite



	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7
FloCarb 10% of Bentonite	8,28	8,37	8,86	8,77	8,87	9,21	9,27

DCS Reduces with progressive cycles



	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7
FloCarb 10% of Bentonite	48,67	51,1	44,59	44,66	40,87	46,58	42,49

Summary of Pouring Cycling test

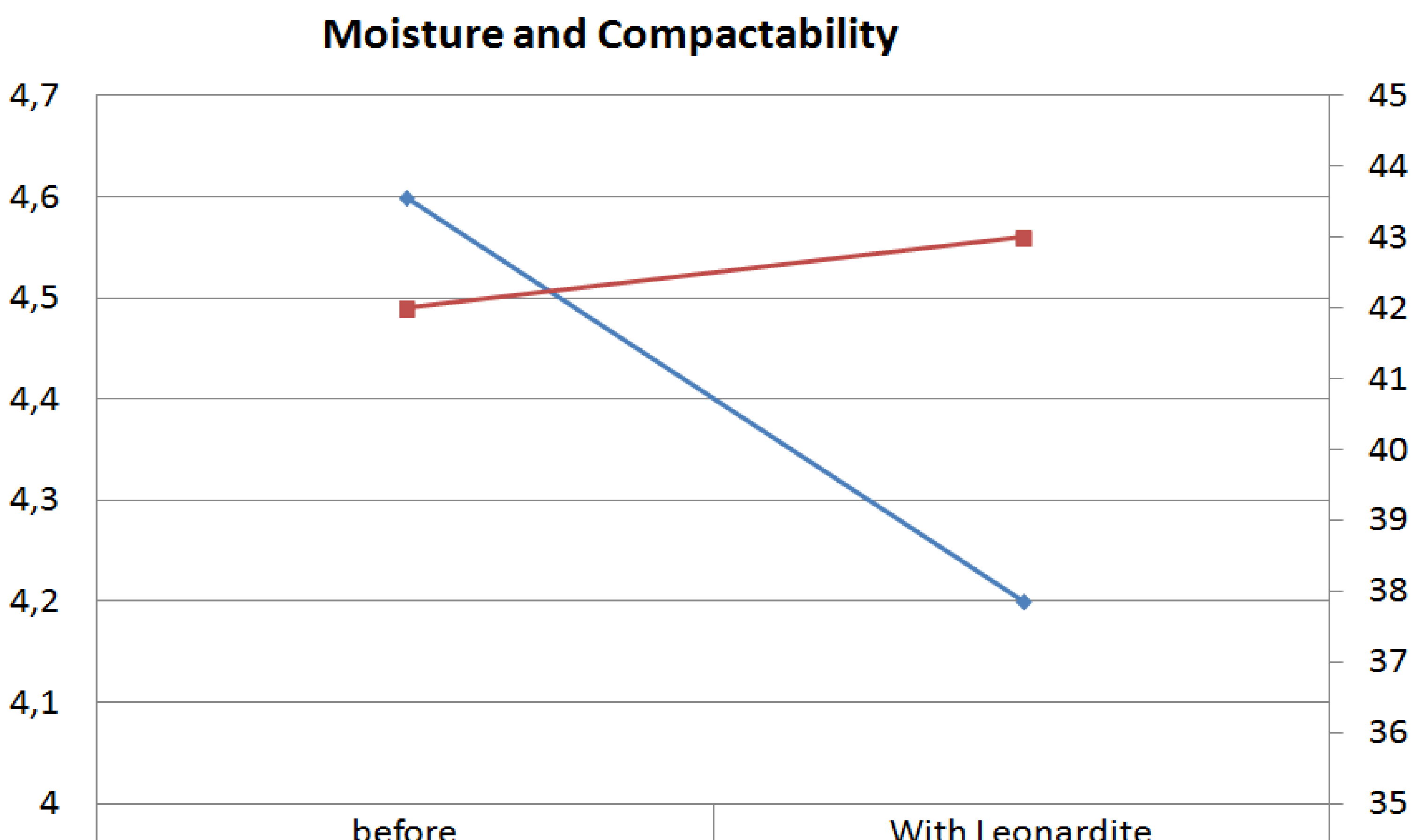
- The previous results help confirm our experiences we find in foundries when introducing FloCarb

1. MB Clay increases – therefore we can reduce the clay addition and achieve equal performance. 30% clay reduction is not unusual
2. Permeability increases – reducing gas entrapment defects
3. WTS strength increases – reducing scabbing and expansion defects
4. Moisture remains stable – this is often a surprise as the FloCarb is a fibrous material. With clay reduction, we often achieve much lower moisture demand for the equivalent CB
5. DCS reduces – helping shakeout properties without impacting on Thermal stability

Summary: Leonardite Impact on Green Sand

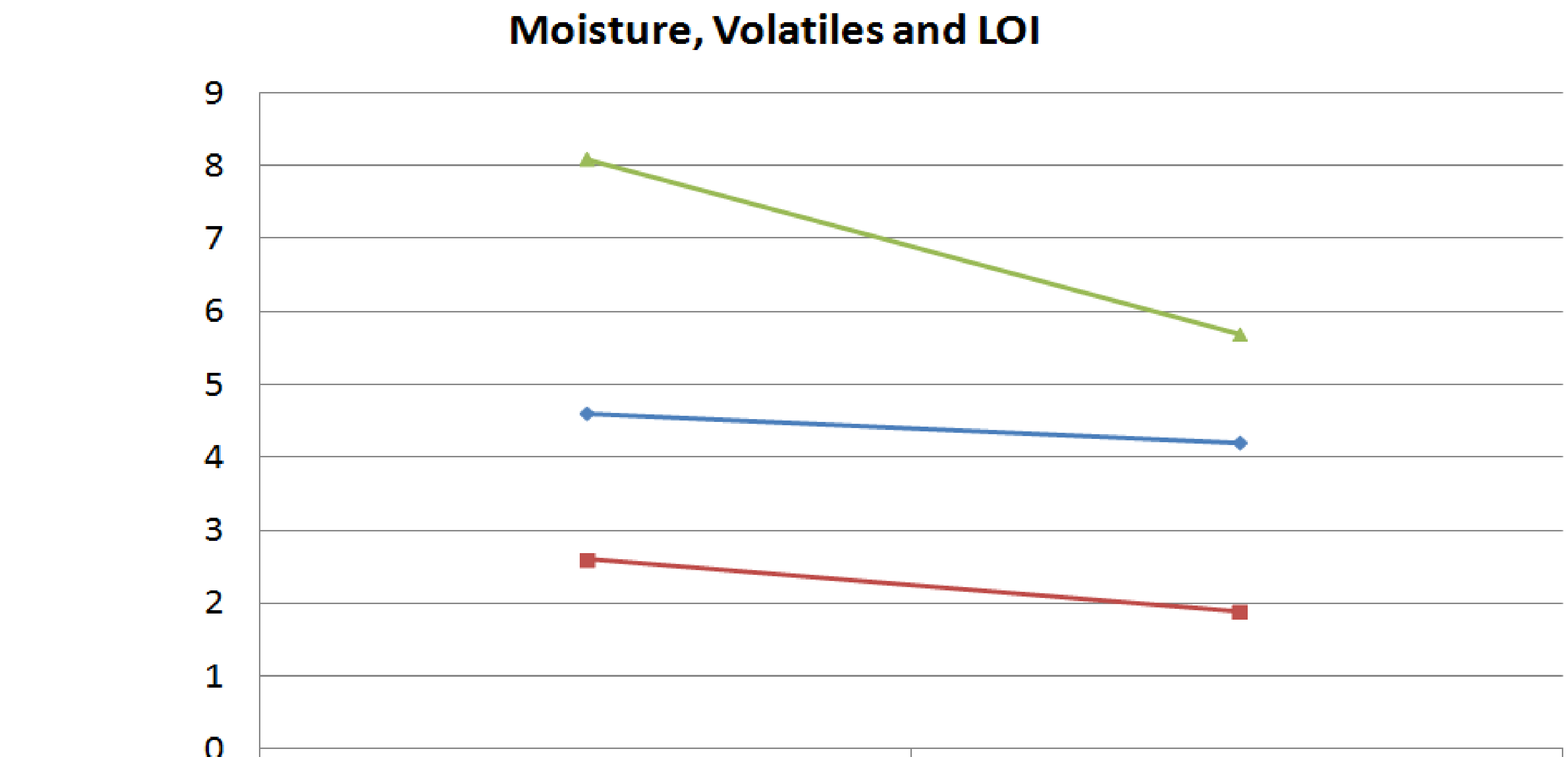
- Green sand flowabilty will improve.
- Green compression strength will increase
- Clay demand will decline.
- Dry compression strength will reduce .
- VCM will remain stable or can be decreased
- Permeability will increase
- Casting peel will remain stable.
- Pattern stripping characteristics will improve
- Shakeout characteristics will improve.
- Moisture retention in hot sand is dramatically improved.

Leonardite Impact: case study in Turkey



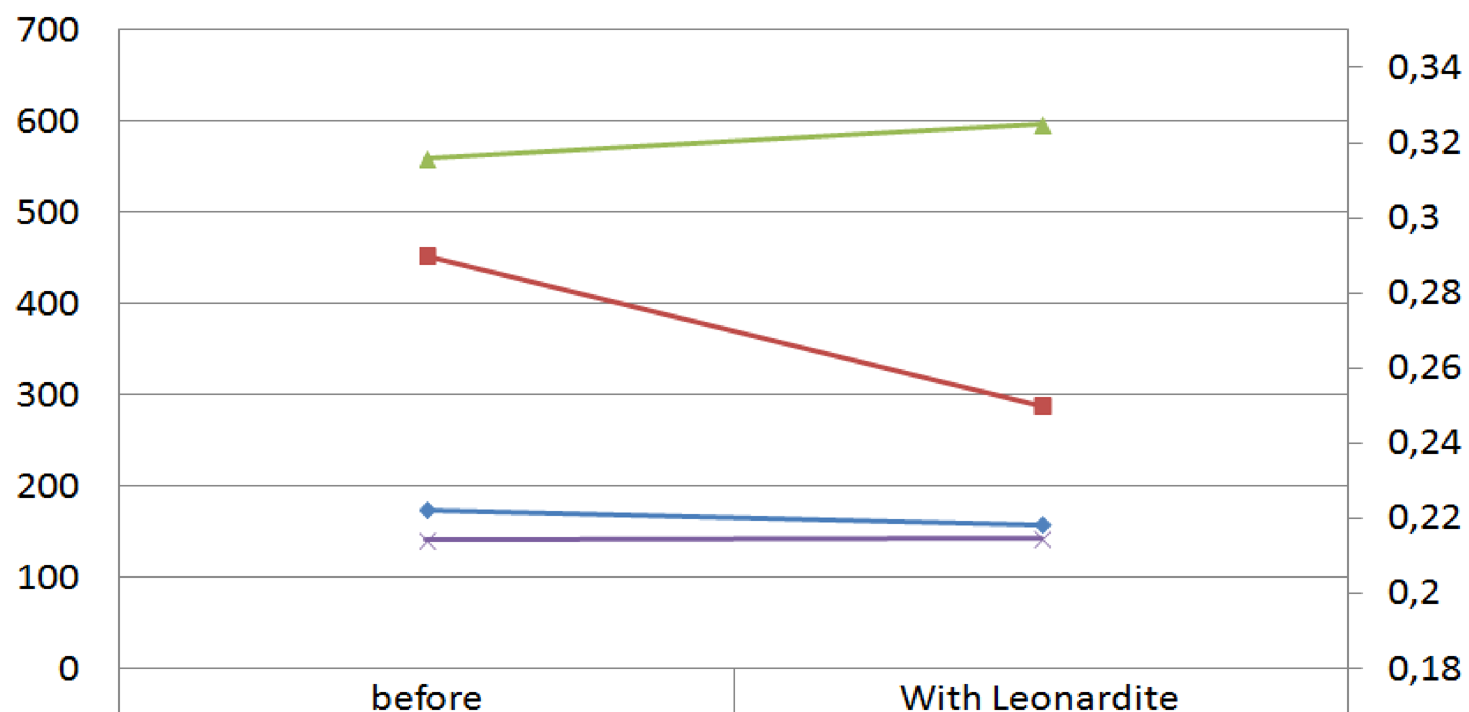
	before	With Leonardite
Moisture(%)	4,6	4,2
Comp (%)	42	43

Leonardite Impact: case study in Turkey



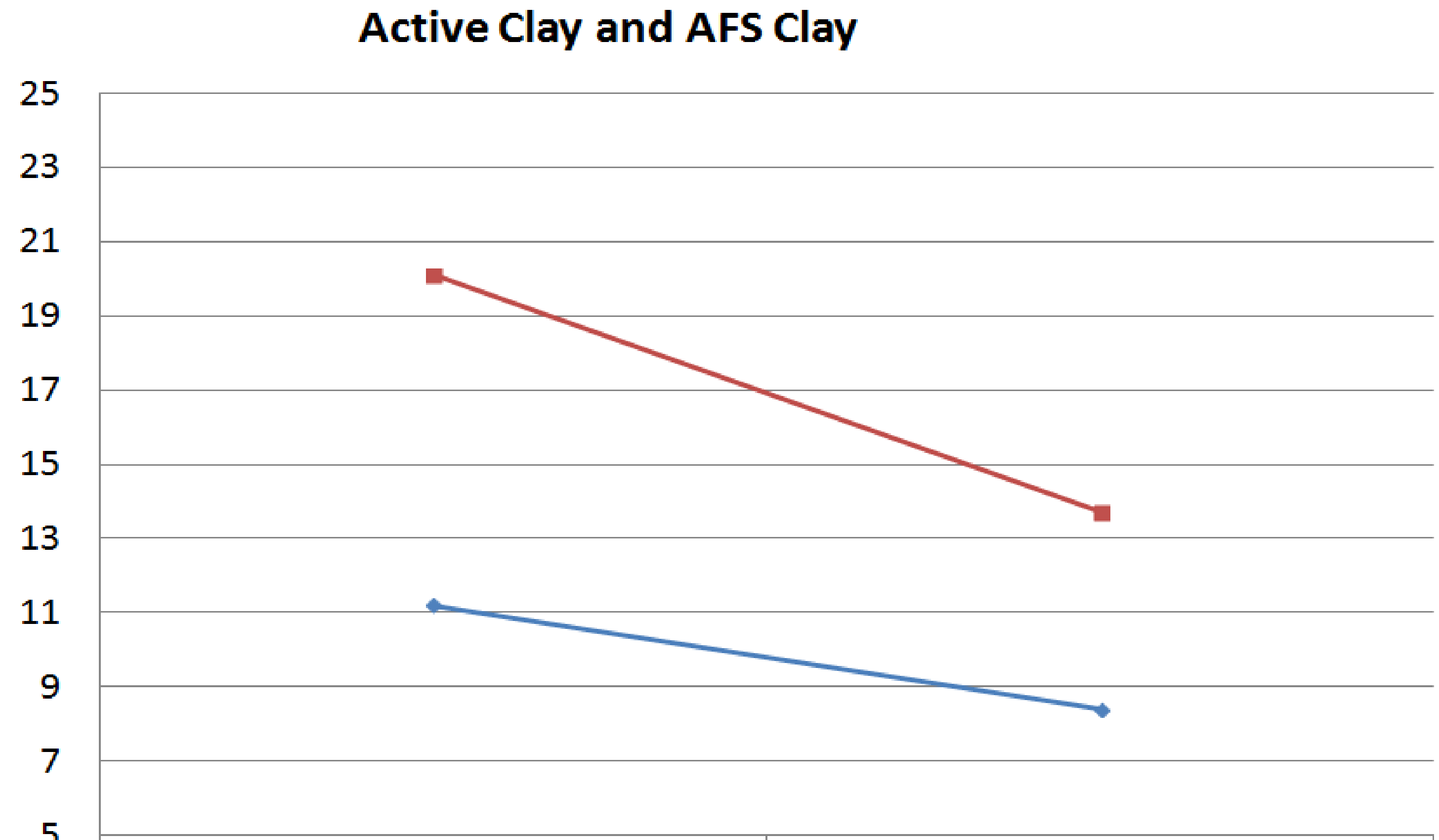
	before	With Leonardite
Moisture(%)	4,6	4,2
Volatile(%)	2,6	1,9
LOI(%)	8,1	5,7

Leonardite Impact: case study in Turkey



	before	With Leonardite
GCS(kn/m2)	174	158
DCS (kn/m2)	560	597
Sample Wgt (g)	141	143
WTS (n/cm2)	0,29	0,25

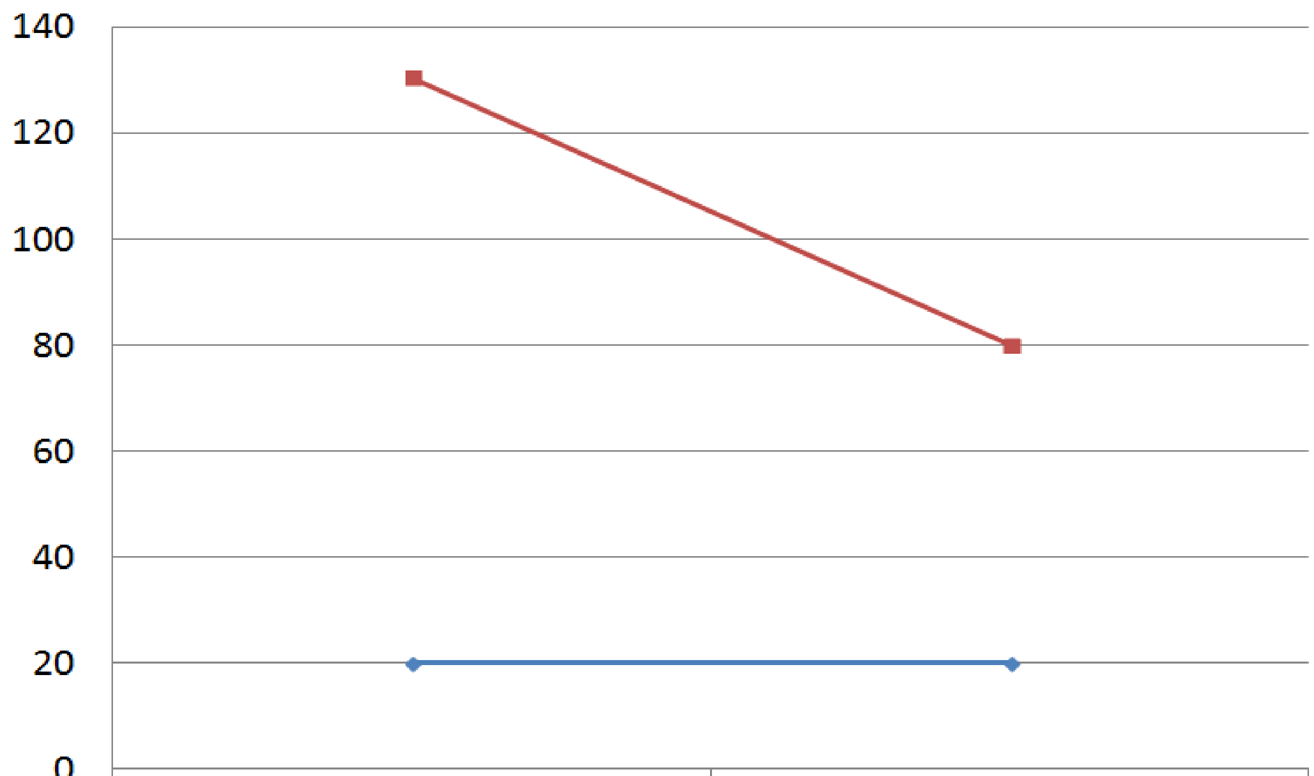
Leonardite Impact: case study in Turkey



	before	With Leonardite
Active Clay(%)	11,2	8,4
AFS Clay(%)	20,1	13,7

Leonardite Impact: case study in Turkey

Bentonite Consumption = 41% reduction



	before	With Leonardite
New Sand (kg)	20	20
Bent/Metal (kg/ T cast)	130,5	80

Effects of using Leonardite as a Seacoal replacement on Mold Gas Emissions - summary

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Testing Summary

- An emission test study was conducted to determine the effect of using FloCarb as a Seacoal replacement for green sand moulding
- The study and testing were conducted by,
  - University of Northern Iowa, Cedar Falls, IA
  - ACC – American Colloid Company

Testing Summary

- The greensand mixtures consisted of the same silica sand, 8% Sodium Bentonite and Carbonaceous additive of 20% of the Bentonite dry weight.
- 4 Recipes where used to compare the effects of substituting Seacoal with FloCarb
  1. 100% Seacoal
  2. 75% Seacoal – 25% FloCarb
  3. 50% Seacoal – 50% FloCarb
  4. 100% FloCarb

Testing Methodology

- The same pattern was used for each testing.
- 3 moulds were produced from each sand batch, and each recipe was cycled 7 times to mature the mix
- The emission testing was conducted on Cycles 6 & 7 – sand mixes stable and coating of grains considered 85%+
- The same metal composition and process used for all test

Testing Methodology

- The emission testing during the casting process remained at constant time for all the test
  - Pouring – 0 to 5 minutes
  - Cooling – 5 to 65 minutes
  - Shakeout – 65 to 70 minutes
- The emission samples were collected and tested by an independent laboratory

Reduction of HAP and VOC – 45% Reduction

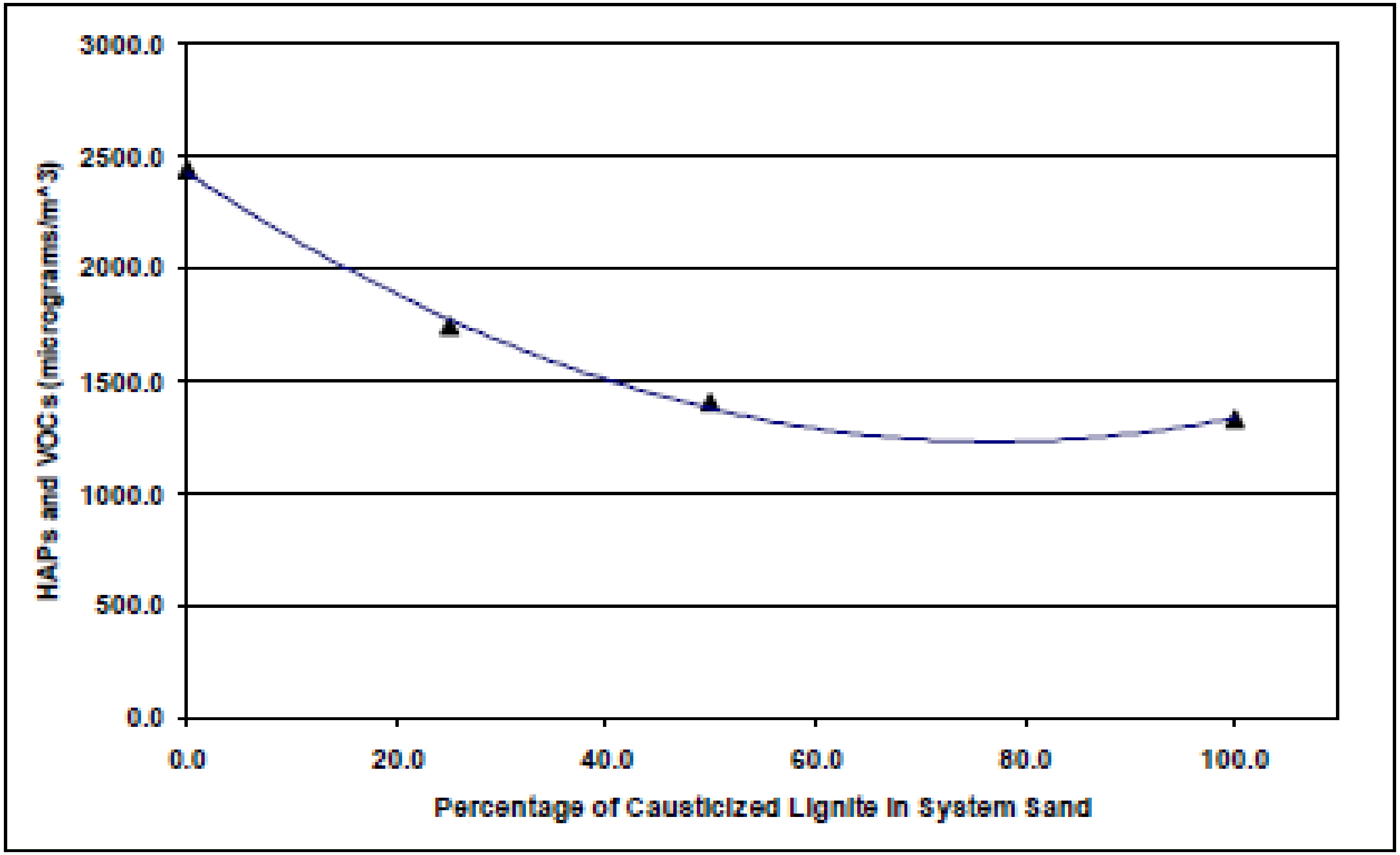

Fig. 4: Reduction of HAP and VOC Emissions as a Function of the Seacoal: Causticized Lignite Ratio

Total Benzene Emissions – 42% Reduction

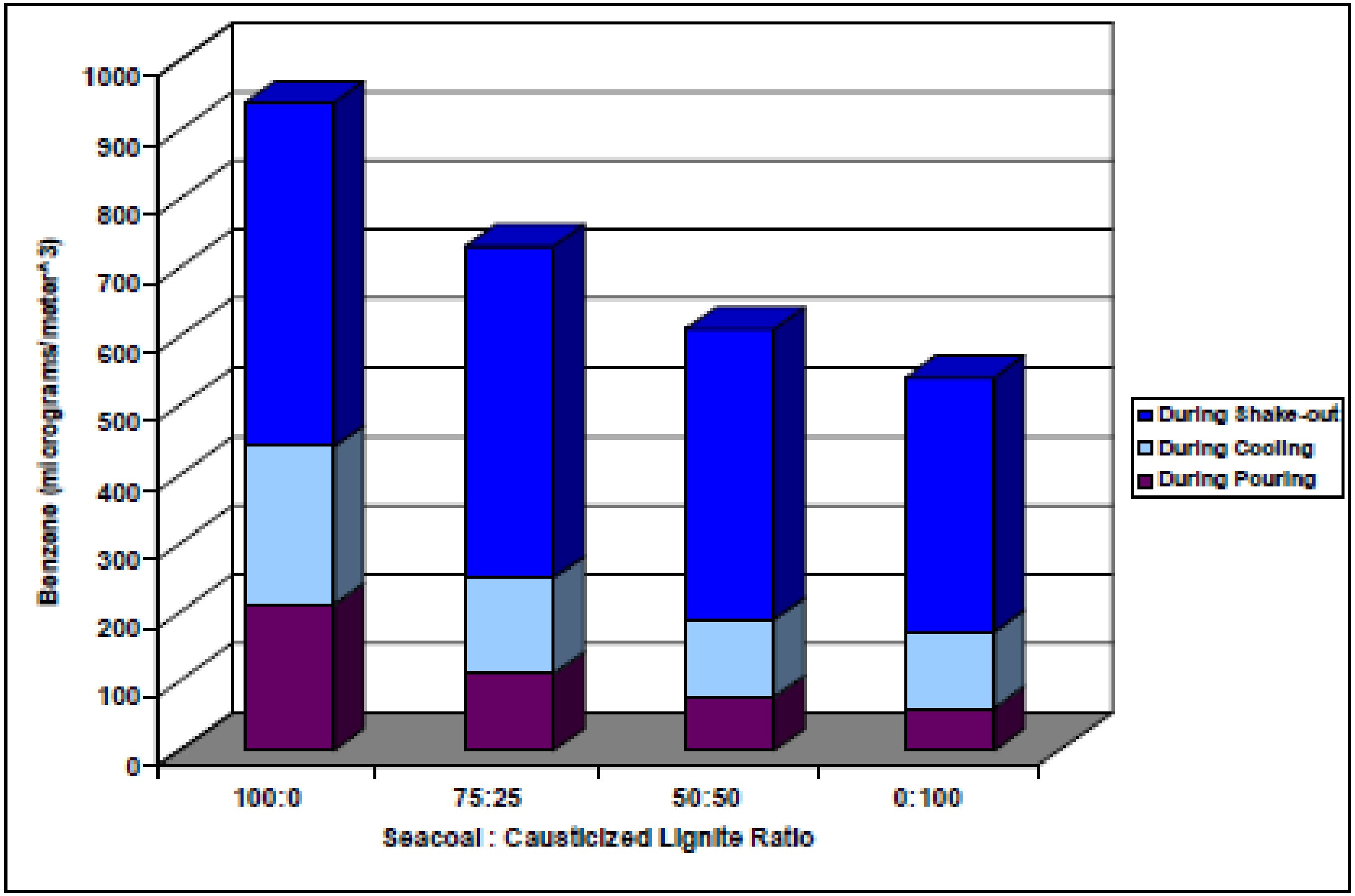

Fig. 5: Total Benzene Emissions as a Function of the Casting Process (μg/m³)

Toluene Emissions – 54% Reduction

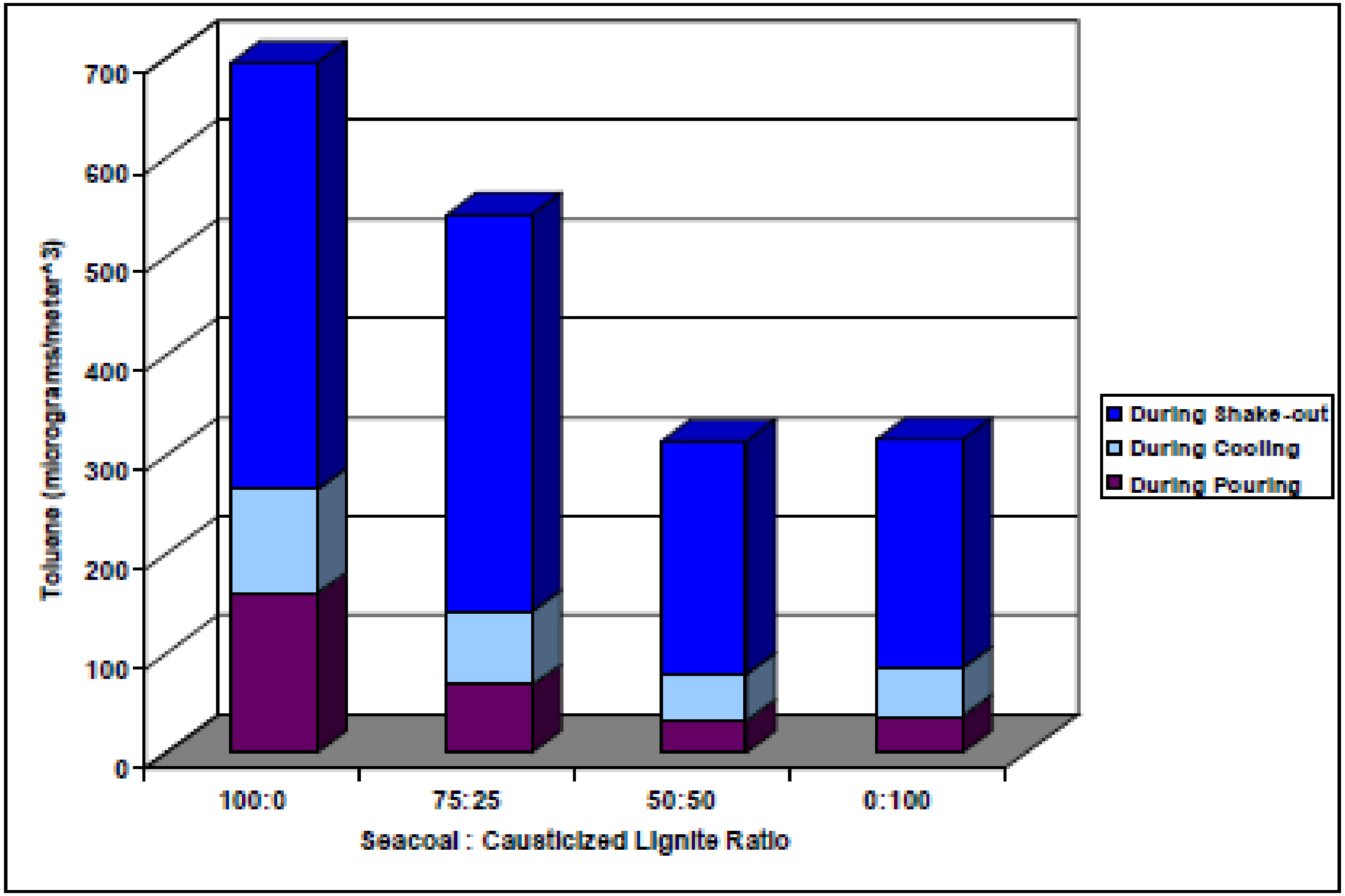

Fig. 6: Total Toluene Emissions as a Function of the Casting Process (μg/m³)

Proportions of Emissions from 100% Seacoal

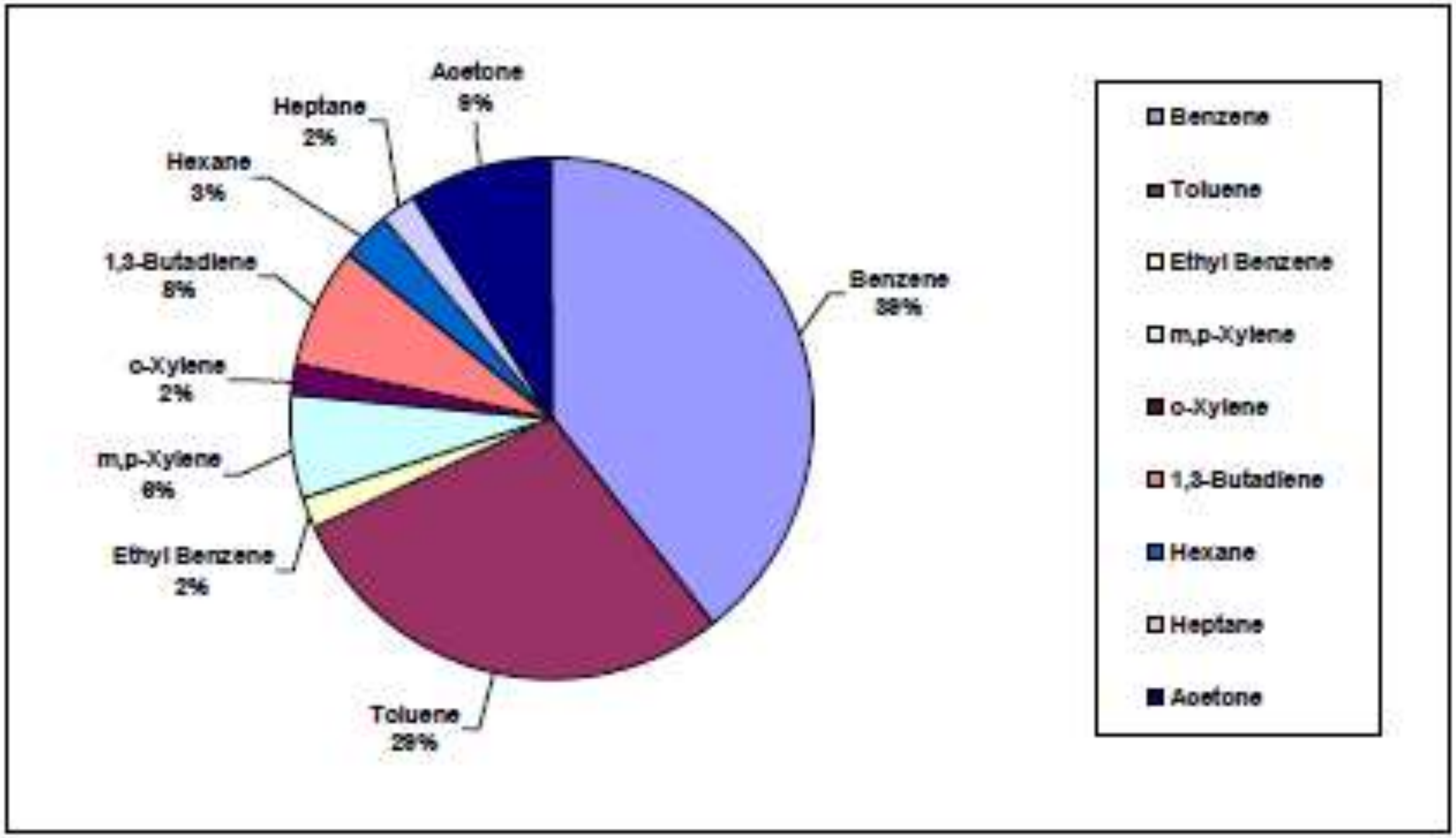

Fig. 7: Proportions of Emissions from 100% Seacoal Green Sand Mixes

Proportions of Emissions from 100% Leonardite

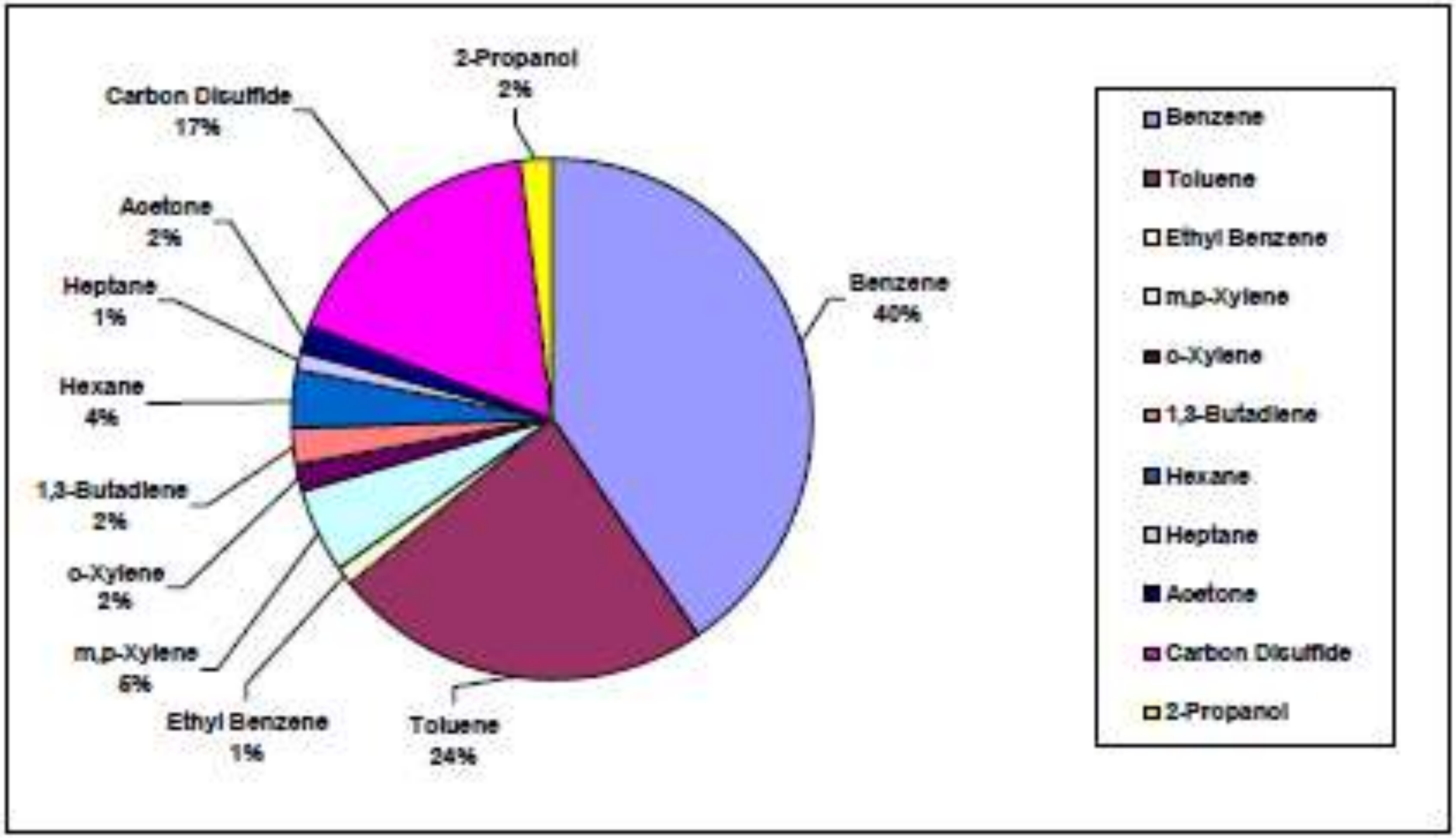

Fig. 8: Proportions of Emissions from 100% Causticized Lignite Green Sand Mixes

Comparison of emissions from green sand test mixes

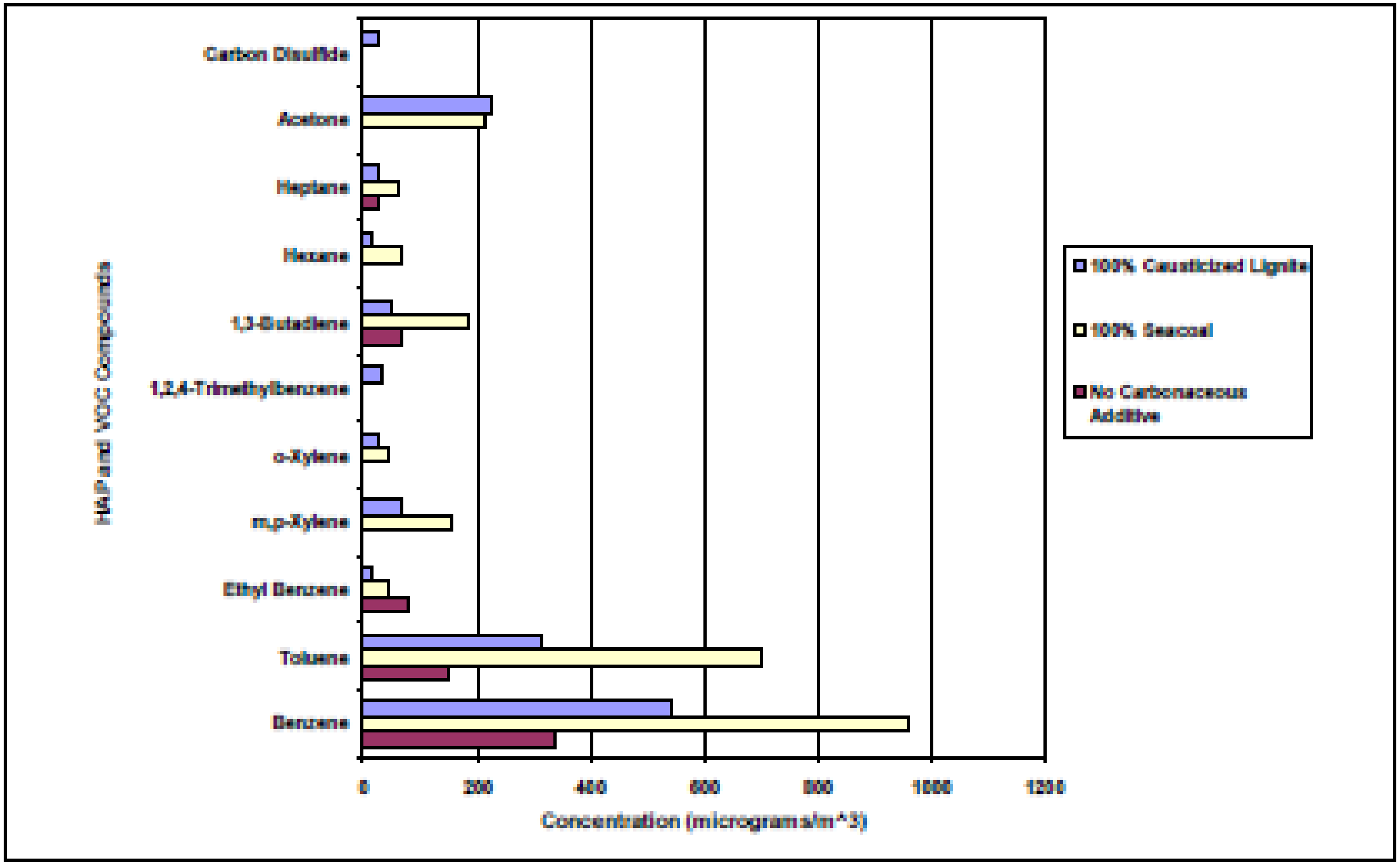

Fig. 9: Comparison of emissions from Green Sand test Mixes (µg/m³)

VCM% for Sand Testing for each recipe – lower for Leonardite

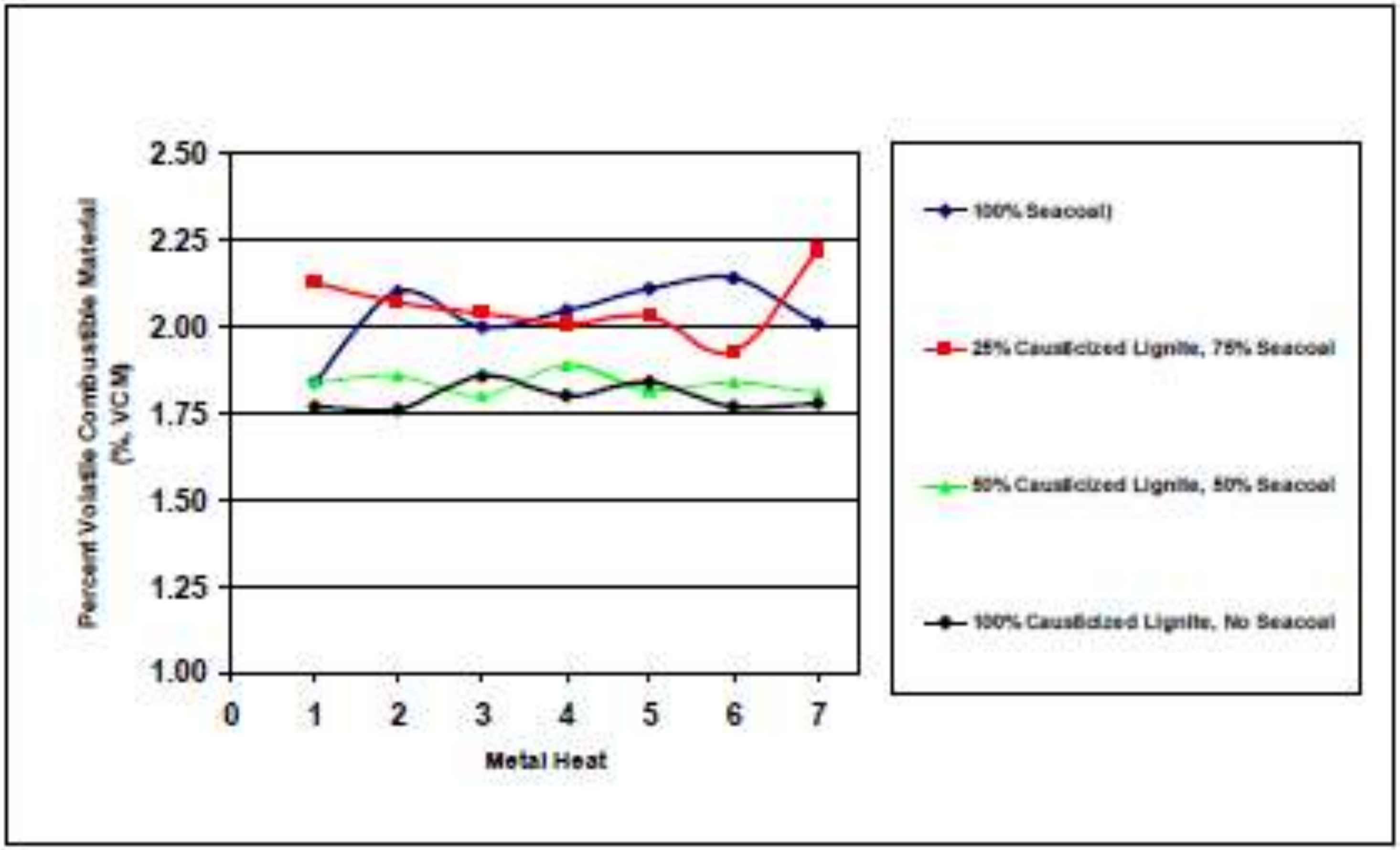

Fig. 12: Volatile Combustible Material (VCM) Results of Lab Testing

LOI% for Sand Testing of each recipe – Lower for Leonardite

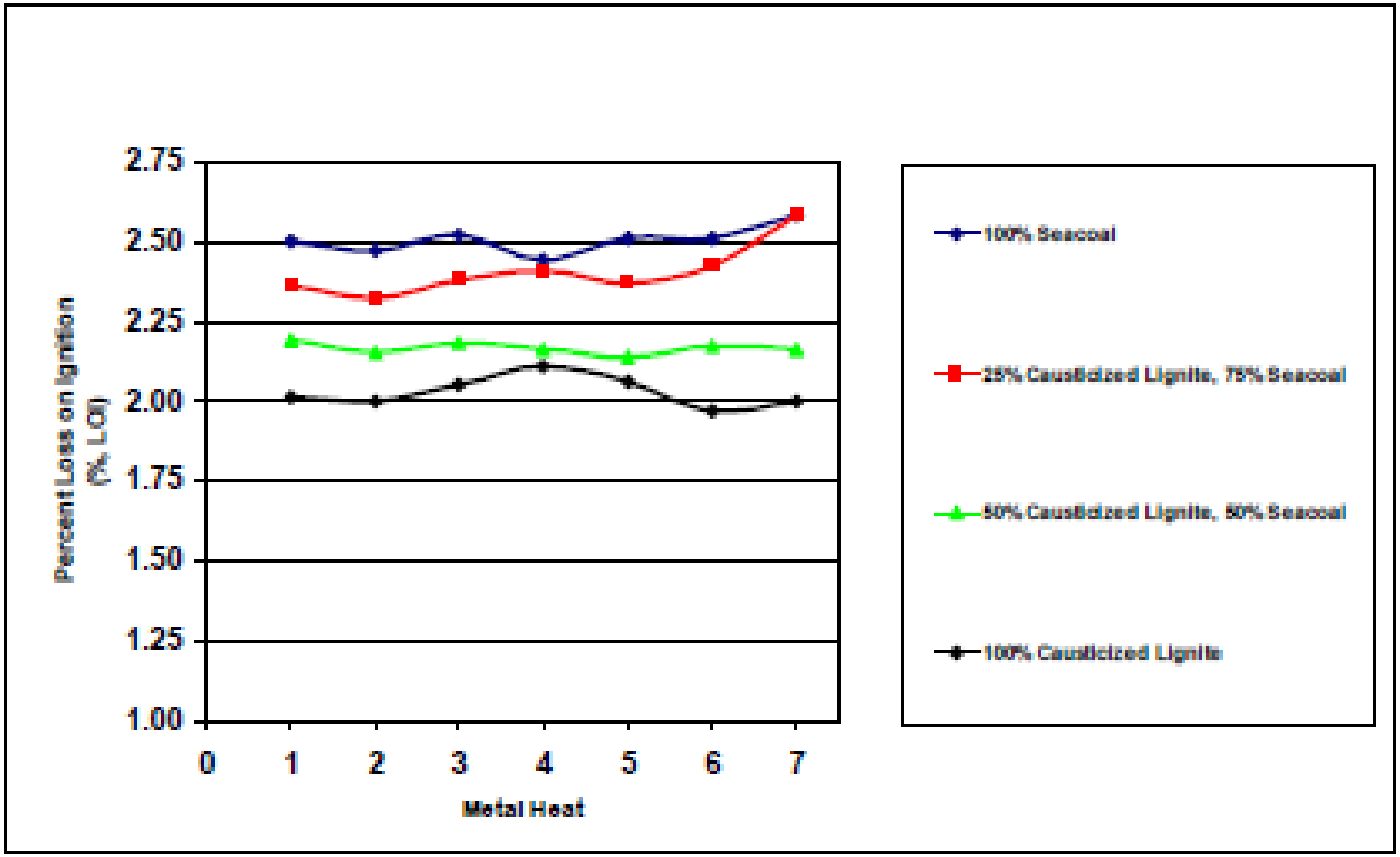

Fig. 13: Loss on Ignition (LOI) Results of Lab Testing

Summary concerning the emissions

- Partial and total substitution of Seacoal with treated leonardite reduced the HAP and VOC emissions by as much as 45%
- Partial and total substitution of Seacoal with leonardite reduced Benzene emissions by as much as 42%
- Partial and total substitution of Seacoal with Leonardite reduced Toluene emissions by as much as 54%
- The mixtures containing Leonardite have a decreased VCM and LOI %
    - This is due to these mixtures requiring lower clay additions to achieve the same MB Clay level – which lowers the Carbonaceous material required.

Conclusion (1/2)

- We have witnessed technical benefits with the use of a specially processed leonardite that offer considerable process improvement and cost savings potential to green sand foundrymen wishing to improve the performance of their mould bonding materials.

- The additional question of BTEX and CO/CO2 emission reduction is summarized and compared to standard green sand recipes.

Conclusion (2/2)

- We have also established the correct ratio of natural sodium to calcium bentonite and the amount of leonardite added relative to other parameters. All of these factors can play a role in determining the degree to which this additive will influence sand properties.

- Leonardite has proven itself to be an effective means to improve sand system performance, foundry environment and casting quality.

Thank you

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