Magotteaux-Test. A rapid test for Evaluation of Reducing conditions in Clinker

Evidence of Reducing Conditions

Brown or yellow rings within nodules react positive when tested by the Magotteaux-Test. Under coaxial illumination these brown zones can in general be identified as a condensation zones of sulfates. The deviation from a concentric shape is attributed to porosity influences

Magotteaux-Test.

A Rapid Test for deducting Reducing Conditions in Kiln by deducting FeO in Clinker produced.

Reduced conditions leads to Wastage of Fuel & undesirable characteristics of Clinker produced.

The Reduced Clinker contains FeO & To test presence or absence of FeO in Clinker.

Two Solution required with two amber glass dropping bottles; Bar magnet & white Porcelain.

Solution A ; -A weigh of 0.25 g of 2.2-bipyridyl & transfer to beaker then add 90 ml of water & 10 ml of Conc. Hydrochloric acid. Stir until reagent had dissolved.

Solution B :-Dissolved 50 g of Tri-sodium Citrate in 100 ml of water ,Then transfer it to amber glass dropping bottles.

Test Procedure:-

Take 5 to 10 milli grams of sample ,Put 2 drop of solution A ,in a depression of white tiles.

Pink color denotes presence of FeO >0.16 % & possible reducing condition in Kiln.

If no Pink color occurred then after 2 Minute add 2 drop of Solution B

Then allowed for 5 Minutes. If Pink color occurred now then less severe. FeO = 0.04 to 0.16%

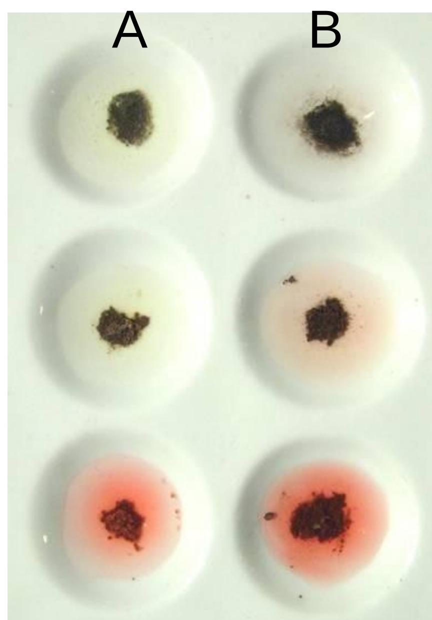
If after then Test Failed then:-

Either Sample is fully Oxidized or Ferrous iron present is low level i.e. < 0.04 % FeO

Discoloration

The Magotteaux test is a rapid test to show the presence of Fe^{2+} in the clinker produced.

The test is based on the reaction between ferrous iron (Fe^{2+}) in solution and 2,2-bipyridyl (solution A) and Tri-sodium citrate (solution B), which results in the formation of a pink complex.



Magotteaux-test negative,

FeO < 0.04%

Magotteaux-test positive with solutions A + B

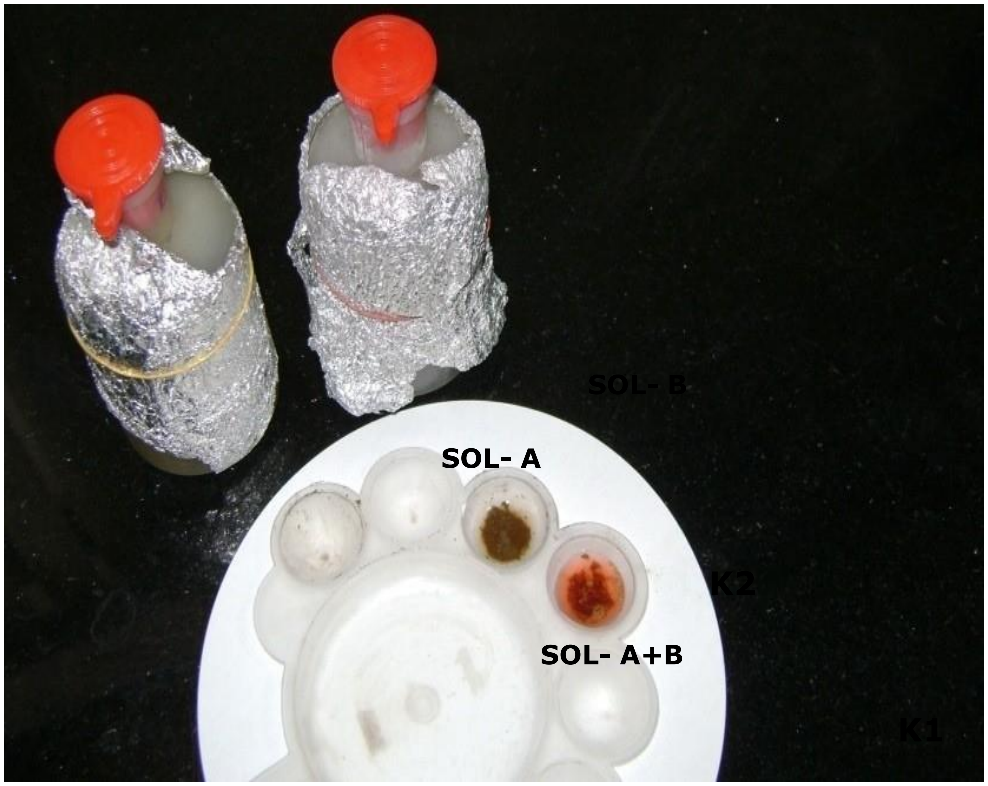
FeO ca. 0.04% – 0.16%

Magotteaux-test positive with solution A alone

FeO > 0.16%

Reducing Conditions

Magotteaux Test



Discoloration

- Reduced clinker is typically brown rather than black or gray.

- Two different types of reduction can occur: atmospheric (gas) or thermal.
- Thermal reduction takes place in the peak temperature of the kiln.
- The brown discoloration is mainly found in the center of the nodules.
- Local reduction occurs when coarse solid fuels drop on the clinker bed and burn on. The general kiln atmosphere may be oxidizing, but part of the clinker gets reduced.

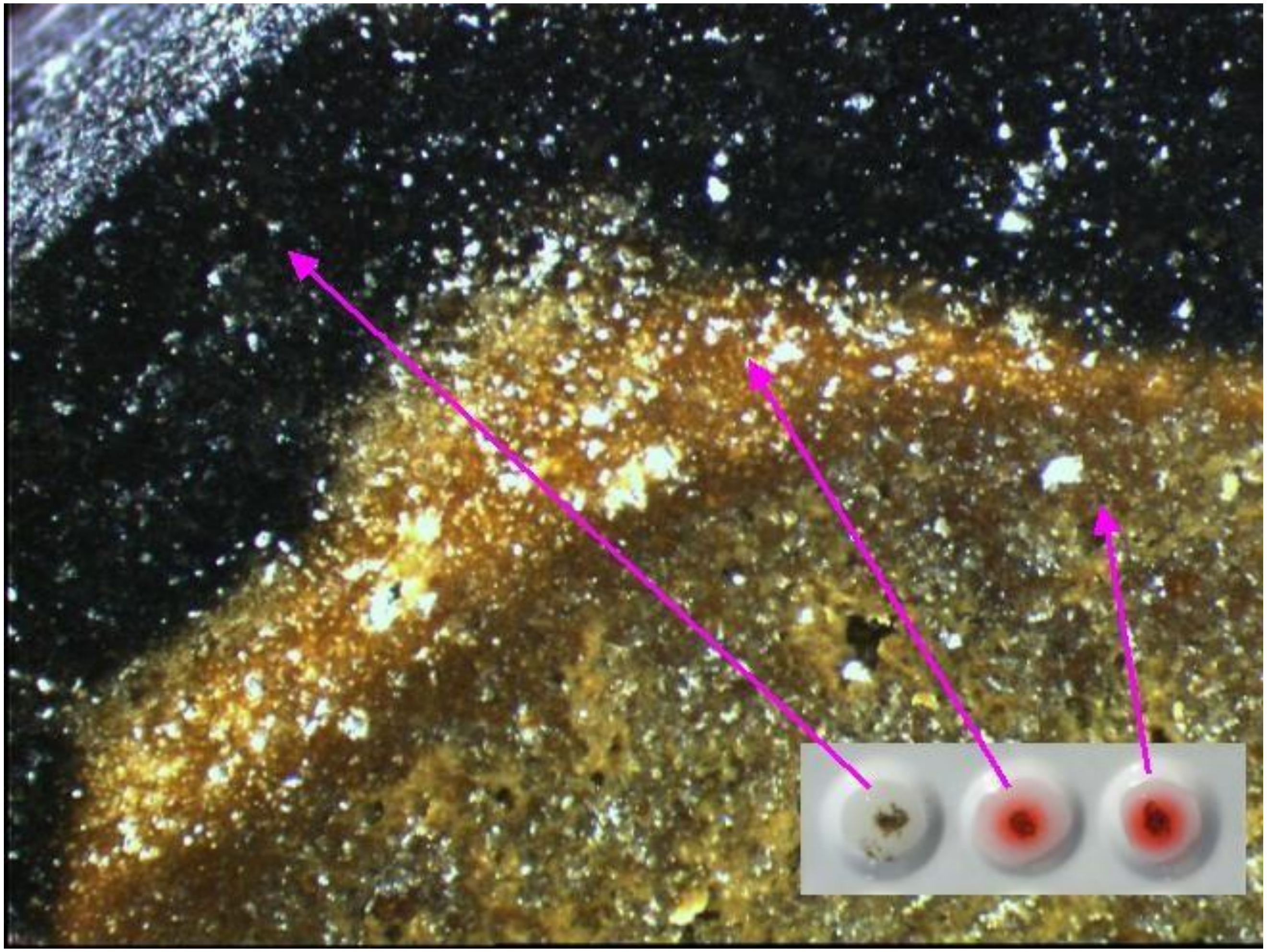
Discoloration

Dense brown cores are indicative of **high maximum temperatures** in the range of 1’500℃ or more. This clinker is very hard to grind and results in brown discolored cement. Magotteaux test positive.

Discoloration

Fuel ash deposits can cause brown spots within nodules. Additional air supply is in general capable to suppress such discolorations. An acceleration of the combustion behavior is also possible by a higher fineness of the applied fuel.

Discoloration



The Magotteaux test is an indicator for the presence of divalent iron.

Chemistry of reducing conditions

Gas based reduction (kiln atmosphere) may happen at any point in the kiln: Fe^{3+} Fe^{2+}.

Low pO_2 can be caused by the presence of carbon, sulfur, pyritic or iron containing compounds, poor flame design, burner pipe out of alignment or non optimized coal fineness.

Fe^{2+} acts as if it was Ca^{2+} or Mg^{2+}.

Fe^{2+} enters the alite, and to lesser extend belite.

LS/C_3S of clinker is increased, making it harder to burn.

The increased ratio of Fe^{2+}/Fe^{3+} enhances the destabilization of alite during cooling, since it accelerates its disintegration to belite and free lime.

Fe^{3+} is rejected from alite, resulting in alite conversion to belite and destabilization of alite

Chemistry of reducing conditions

- Lack of Fe^{3+} reduces ferrite generation, while increasing aluminate content.
- Fe^{2+} displaces the gray coloring Mg^{2+} (and Ca^{2+}) ions in ferrite (C_4AF), leading to a brown Fe^{2+}- C_4AF. This material is responsible for the lighter clinker color and hence the cement color.

- The normal, dark color of clinker is due to the ferrite phase, which in the form that commonly exists in clinker is a semiconductor and strongly absorbs light of all wavelengths. The semi conductivity and color have been attributed to the presence of oxygen vacancies resulting from the substitution of tri-positive ions by Mg^{2+} together with electrons released by the oxidation of Fe^{2+} to Fe^{3+} (and even up to Fe^{4+} - it appears to require a small fraction of Fe^{4+} for the dark color) that occurs on cooling. If more than a small proportion of the iron remains as Fe^{2+}, the clinker is yellow to brown.

Scrivener &v Taylor, World Cement Research and Development, August 1995

Chemistry of reducing conditions

- The equilibrium existing in the burning zone of the kiln is such that a significant proportion of the iron is necessarily present as Fe^{2+}, even if the kiln atmosphere is normal. Oxidation occurs during cooling, and may be incomplete in the centers of large nodules.
- The presence of light colored centers of large nodules therefore does not necessarily imply the existence of reducing conditions in the kiln; it may only denote a decreased degree of oxidation during cooling.

- Re-oxidation in the cooling zone of the kiln reverts Fe^{2+} Fe^{3+}

  Ferrite phase color is reversible and with re-oxidation becomes dark brown again (clinker needs to leave the kiln at a temperatures of at least 1250℃).

Scrivener &v Taylor, ZKG, 1/1995

Chemistry of reducing conditions

- Clinker cooling in the kiln and in the cooler should be fast.
- However, if the clinker is reduced and cooling is “too” fast, then there is not enough time for re-oxidation
- Coal ash, if deposited heterogeneously, may stop re-oxidation by forming a molten skin around the clinker nodule.

- Clinker with a high SR (low liquid phase, high porosity) is easier to re-oxidize than dense clinker with a low SR (high liquid phase).
- If clinker nodules are dense (low SR, high liquid phase) and/or big (> 2.5 cm), then oxygen can not penetrate the clinker center and re-oxidize before cooling below the critical 1250 ℃

Chemistry of reducing conditions

Reducing conditions lead to more sulfur volatilization:

$K_2SO_4 \leftrightarrow$	$K_2O + SO_2 + ½\ O_2$
O_2 excess:	reaction moves to the left
O_2 deficit:	reaction moves to the right

The remaining alkalis with higher ion radius than Ca^{2+} are built into the C_3A lattice, forming the unfavorable orthorhombic C_3A.

Reduced clinker contains less sulfates.