

# Mineral Deposits in Pulp Bleaching

**Abstract:** *With the increasing closure of bleach plants in chemical pulp mill, many minerals accumulate in the process, which may lead to deposits. These plug the washing devices and severely impact the productivity of fiber line.*

*This paper deals with the conditions under which the deposit is formed and various methods to minimize the deposit formation.*

**Key Words:** *Bleach plant, deposits, scale, calcium carbonate, calcium oxalate, calcium sulfate, barium sulphate, solubility, pH*

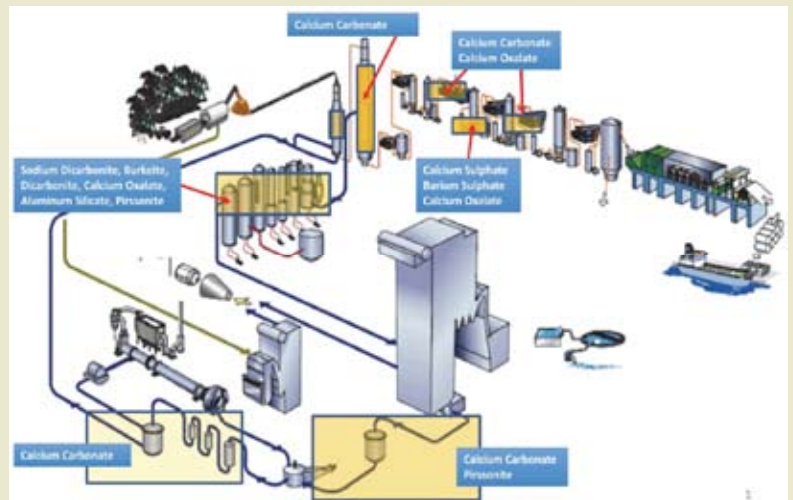


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## Introduction

In a pulp mill of capacity of about 500 tons/day, based on hardwood about a thousand of kilogram of calcium passes a pulp mill and



*Fig 1: Typical inorganic scale potential in Kraft cycle*

bleach plant each day. If not properly managed this may precipitate onto various surfaces as shown in Fig 1, resulting in operation upset and increased cost.

With a good understanding of chemistry behind scaling, minor adjustments can be made in operating conditions to minimize scaling.

### Why does it scale?

Three conditions are necessary in order to form scale:

1. Supersaturation,
2. Accelerated kinetics, and
3. Optimum substrates (surfaces).

1. **Supersaturation** occurs when dissolved ions such as  $\text{Ca}^{+2}$ ,  $\text{CO}_3^{-2}$ ,  $\text{C}_2\text{O}_4^{-2}$ ,  $\text{Na}^{+1}$ ,  $\text{Ba}^{+2}$ , and  $\text{SO}_4^{-2}$  increase in concentration to levels that exceed the normal solubility limits of the process stream. Table1.

**Table1: Solubility of compounds**

Compound	Formula	Solubility at 18°C
Calcium carbonate	$\text{CaCO}_3$	0.014
Calcium oxalate	$\text{CaC}_2\text{O}_4$	0.0074
Sodium carbonate	$\text{Na}_2\text{CO}_3$	75
Barium sulphate	$\text{BaSO}_4$	0.0025
Calcium sulphate	$\text{CaSO}_4$	2.4
Sodium sulphate	$\text{Na}_2\text{SO}_4$	50

It should also be mentioned that some scale species exhibit what is known as inverse solubility. Some common species in a pulp mill that exhibit inverse solubility include calcium carbonate ( $\text{CaCO}_3$ ) and calcium sulfate ( $\text{CaSO}_4$ ). In other words, as temperatures rise, these species are more prone to come out of solution and deposit. This indeed presents an added challenge in hot systems such as digesters and evaporators.

2. **Accelerated kinetics** is to describe conditions that are conducive to scale formation. These can include temperature shocks, intense mechanical and hydrodynamic shear forces (e.g. pumps): Fig.2 Also, optimum pH conditions, and sudden changes in pressure.

3. **Optimum substrates** refer to the various non-uniform surfaces in the pulping process that are conducive to scale formation. These non-uniform surfaces include heat exchanger tubes made rough by corrosion or erosion, washer face wires (Fig.3), and screen plates. These surfaces provide a mechanical “foothold” for scale microcrystals to begin growing.



Fig2: Scale in MC pump



Fig3: Scale in wire

Scale that has accumulated from one type of component can form an excellent base for other scales to grow on. For example, calcium carbonate scale in black liquor evaporation is often the foundation of scale formation and other scales such as sodium carbonate and burkeite, which build upon the Calcium Carbonate matrix.

### Scale Deposits in Bleach Plant:

The fundamental reason for scale is trace metal ions entering the bleach plant, originating from wood, Table2. System closure has further aggravated the severity of scaling in bleach plants. Hardwood contains higher concentrations of trace metals than softwood by a factor of two or more, Table 2&3, thus causing more problems in hardwood bleach plant. Scaling occurs at several places like first Q –stage of TCF process, acidic and alkaline stages of bleaching process, filtrate tanks, washer filter, wires, shower nozzles, repulper screws, pumps, stock lines and on-line instrumentation.

**Table 2: Trace metals associated with various raw materials**

Particulars	Bagasse	Wheat Straw	Rice straw	Tropical hardwood
Ash	2.3	9.5	18	0.3
Silica	1.8	5.8	11	0.2
Potassium	0.2	1.8	2	<0.1
Calcium	0.23	0.12	0.18	0.15
Chlorides	<0.1	0.88	0.94	<0.1

expressed as % oven-dry basis

**Table 3: Comparison of trace metals in wood & bark in various raw materials**

Species	Wood*		Bark*	
	Ca	Mg	Ca	Mg
Birch	430	140	5,900	430
Pine	700	150	4,950	656
Spruce	870	120	11,300	890
Alder	760	210	6,370	900
Oak	470	62	22,900	690
Eucalyptus	1000	370	15,200	1,850

Majority of scales found in bleach plant are:

- Calcium carbonate, Fig. 4
- Calcium oxalate, Fig. 5
- Barium sulphate

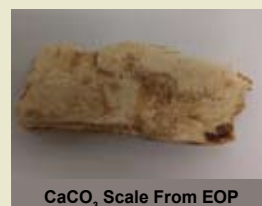


Fig4:  $\text{CaCO}_3$  scale pipe to EOP

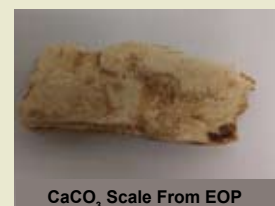


Fig5:  $\text{CaC}_2\text{O}_4$  scale

1.a. Calcium Carbonate Scale:

As can be seen from Fig6, calcium carbonate scale is common in bleaching stages such as extraction, peroxide and hypochlorite, where pH exceeds 9.

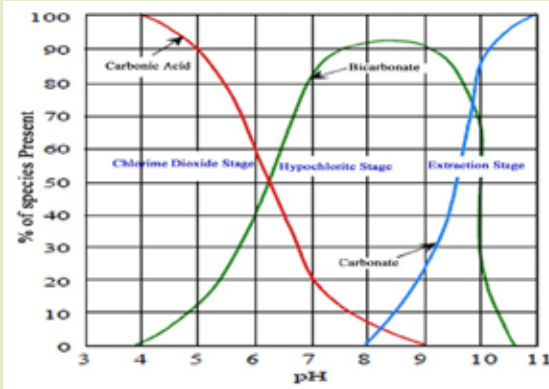


Fig6: scaling at various pH

Calcium carbonate is the result of the presence of Ca from the wood, to a lesser degree the mill water and from filtrate recycle, combined with carbonate from the process. Filtrate recycle as shower and/or dilution water – depending on which stage is the source – D<sub>1</sub> and/or E<sub>2</sub> – will be a major source of deposition materials. D stage filtrates will contribute a large amount of soluble Ca – which will come out of solution at higher pH. Fig.7.

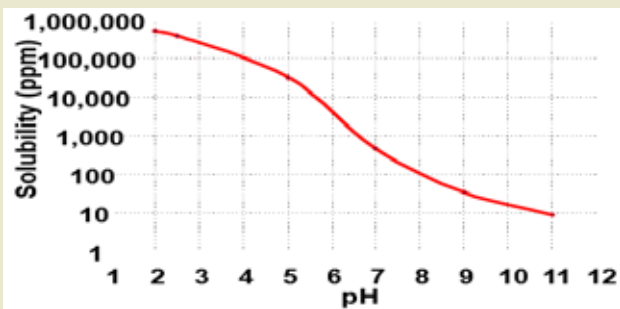


Fig7: Effect of pH on CaCO<sub>3</sub> solubility

Deposition can be found on reaction vessels, pumps, face wires, wire backing channels, screw conveyors, stand pipes – any location after the change in pH from acid to alkaline conditions. The high pH causes the CaCO<sub>3</sub> to deposit out of solution. Shear and temperature (CaCO<sub>3</sub> is inverse soluble to temperature) will make the scale form more rapidly.

Operating Conditions that reduce the scale potential of Calcium Carbonate are:

- Bark contamination of less than 0.5%, which minimizes calcium & oxalate content.
- Suspended solids of less than 25ppm in white liquor will minimize the CaCO<sub>3</sub> in the process.
- Chemically treated shower water to tie up Ca<sup>++</sup>
- Part of filtrate should be severed to remove Ca<sup>++</sup> from the loop &.
- Use of antiscalant chemicals

1.b. Calcium Oxalate Scale:

Calcium oxalate is probably the most common scale problem observed in bleach plants. In many mills, oxalate scale problem appears shortly after switching the bleach plant to elemental chlorine free bleaching. Common bleaching stages, where oxalate could form are chlorine dioxide, hypo and ozone stages where pH is in between 3 -9. Fig.8.

However, with high levels of oxygen in peroxide and oxygen stages, oxalate scale can even be found at pH11 (EO, P & O<sub>2</sub> delignification stages). Oxalate scale is highly pH dependent. Any swings in pH can quickly lead to Calcium oxalate scale.

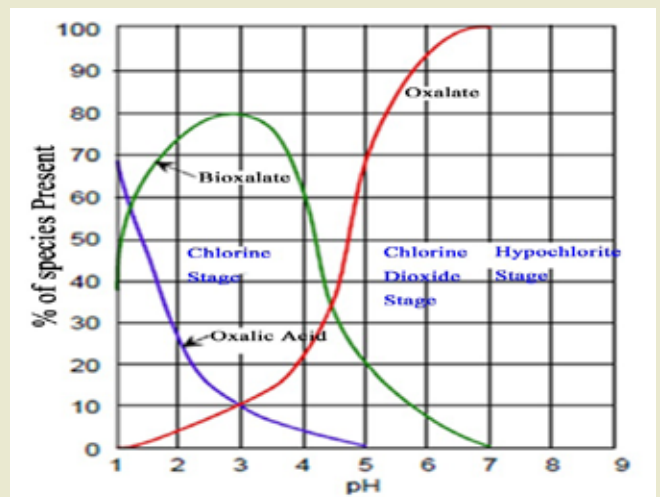


Fig8: Scaling at various pH

Calcium dissolves once the pH drops below 7. When calcium is dissolved, it is capable of reacting with oxalic acid to form calcium oxalate.

Oxalic acid is found in wood and is also formed in the pulping process, but conditions in the digester strongly favor calcium carbonate formation thus the oxalate is left in solution and is removed in brown stock washing. The majority of the oxalate in a bleach plant is formed by oxidation of lignin and hemicellulose during bleaching. All oxidizing stages generate oxalic acid as shown in Figure 9.

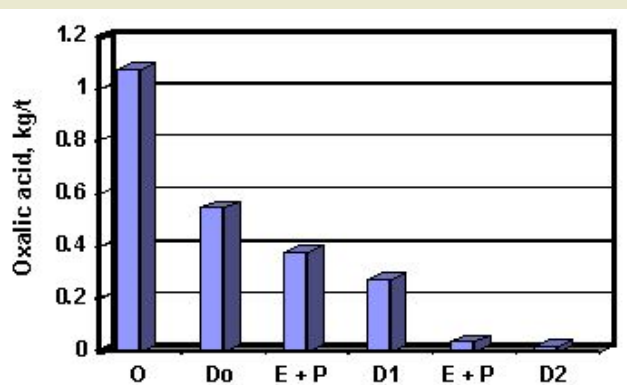


Fig9: Oxalic acid formation in ECF bleaching sequence

Operating Conditions that reduce the scale potential of Calcium Oxalate are:

- Bark contamination of less than 0.5%.
- First acid stage vat pH below 2-2.5. This keeps Ca<sup>++</sup> soluble and able to wash out from the system
- Use of antiscalant

#### 1.c. Barium Sulfate scale:

Of the three common mineral scales encountered in bleach plant barium sulfate scale is the most difficult to remove and the most difficult to prevent too. The major source for barium in the bleach plant is the trace amounts found in wood. Barium, however, is truly a non-process element.

Most of the barium present in the pulping process exists in the digester as barium carbonate. Barium carbonate dissolves in bleach plant when pH drops below 7 and if, barium and sulfate concentrations (liquor carry over and sulfuric acid used in pH adjustment prior to chlorination stage) are too high, it begins to precipitate as barium sulfate.

However, barium sulfate solubility increases by at least one order of magnitude as the temperature rises

from room temperature to kraft cooking temperature, and barium sulfate becomes more soluble than the carbonate salt at approximately 160°C.

Operating conditions that can reduce barium sulfate tendency include:

- Eliminate use of spent acid (sodium sesqui-sulfate) for pH control in the D<sub>0</sub> stage
- If this is not sufficient, work on improving brown stock washing. Remove residual carryover sulfate, sulfide, and lignin-bound sulfur from the pulp.
- Acid stage vat pH below 2.0
- Partly sewer the filtrate
- Chelant boil-out at regular intervals to keep wire open.
- Use of antiscalant

## Summary

Scaling in Bleach plant is an unavoidable phenomenon, caused by the presence of trace metals, coming into the system with wood. The extent and severity of scaling depends on the availability of metal ions and process conditions.

Following are the ways to minimize deposit formation via process optimization:

- Control bark content: less calcium, barium and oxalate
- Improve causticization efficiency, to reduce CaCO<sub>3</sub> in white liquor
- Maintain low suspended solids in white liquor to minimize CaCO<sub>3</sub>
- Improve brown stock washing to reduce caustic and Sulphur containing compound and barium.
- Maintain D<sub>0</sub> pH to 2.5-2.8, to minimize calcium oxalate
- Purge D<sub>0</sub> filtrate partially to avoid calcium /barium build up
- Avoid running countercurrent washing in bleach plant
- Avoid controlling D<sub>0</sub> pH with spent acid from ClO<sub>2</sub> plant

Seldom, the process requirements and conditions favoring a “low scaling” environment are contradictory, making use of scale control chemical, a necessity.

Having said that, under Indian condition where raw material availability is limited, hardwood is often used with bark, non- wood is also utilized, usage of scale control chemicals work best to minimize scaling.

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