Bulletin 5

Silicate Chemistry Key to Solving Mill Scale Problems

Gerard Le Fevre and James R. Moran

Solving scale problems at Millar Western Pulp Ltd. Uncovered some of the complex chemistry of scale formation

Mill managers moan when they see scale forming on their equipment. The sources and causes of scale on equipment are many and varied. More and more mills are moving to hydrogen peroxide bleaching processes that include sodium silicate, and silicate scale can sometimes be a problem. But silicate scale is far from a necessary evil. With proper design, operation and maintenance procedures as well as some help from plant chemists and engineers, scale can be eliminated.

At the Millar Western mills in Whitecourt, AB, and Meadow Lake, SK, Canada, scale was a problem from startup of these sister mills in 1988 and 1992, respectively. In 1993, Millar Western and PQ Corp. began a scale control program that would control chronic scale for both mills and provide a real-world test for scale-control methods developed in the PQ Corp. R & D labs located at the National Silicates offices near Toronto, ON. National Silicates is a wholly owned Canadian subsidiary of Pennsylvania-based PQ Corp.

(Before) Build-up of silicate scale on Thune® Dewatering Press.

Two of the Thune® Dewatering Presses at Millar Western's Whitecourt mill.

(After) Dramatic reduction of scale build-up after optimization of ratios of Epsom salt and sodium silicate at the bleaching stage.

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PQ Corporation is a privately held global enterprise operating in 20 countries, with annual revenues in excess of $500 million. PQ is a leading producer of silicate, zeolite, and other performance materials serving the detergent, pulp and paper, chemical, petroleum, catalyst, water treatment, construction, and beverage markets.

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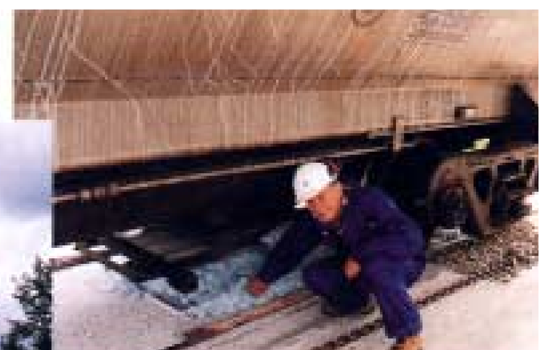
Within two years, the program of understanding and fixing the scale problems has overcome the scale-related difficulties at the Millar Western mills. Just as important, the experience at these mills has pointed out answers to scale problems that can be used at other mills to reduce scale formation and cut maintenance costs.

THE SCOPE OF THE SCALE PROBLEM

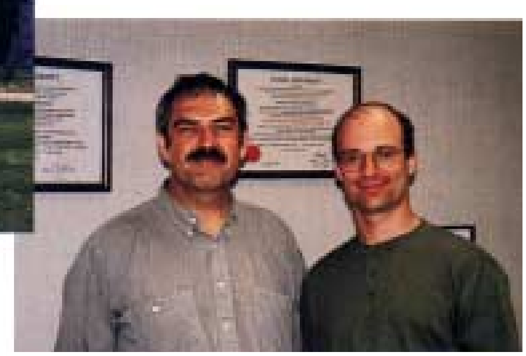
As more and more mills use peroxide in their bleaching sequences, scale can become a problem that mill managers mention more often and with more frustration. To begin to determine the scope of the problem we convened a meeting of technical managers in a hotel away from their mills. We wanted to hear about their scale problems away from the pressure of day-to-day operations. The meeting was chaired by a facilitator who was not familiar with mill scale problems but who could keep everyone talking and working together. At the end of the two-day session we had a clearer picture of the scale problem-at least within the experience of technical managers of thermomechanical mills in Western Canada. The results:

1. Scale is not one problem but several problems. Therefore, several answers would be needed in each mill to solve the scale problem.
2. Scale problems varied by process as well as by product. Market pulp operations had more scale-prone equipment in the process than did integrated mills.
3. Four problem areas topped the “To Do” list. 1) silicate holding tank and related piping; 2) bleach liquor makeup system and related piping; 3) mixers; and 4) presses and dewatering equipment.



Dale Penney, senior facility technician, grabbing a sample of sodium silicate, which was just delivered to the National Silicates’s satellite plant.

National Silicates Ltd. operates a satellite plant at Whitecourt.



Gerard Le Fevre was teamed with Whitecourt’s Technical Supervisor Gerard Orlowski to unravel Millar Western’s scale problem.

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From the meeting and from our own research we determined that all of the scale contained silicate but the specific cause, and thus the specific solution needed for each problem, was independent at each stage of the process. We also surveyed managers of other mills for a total of eight variations of the thermo-mechanical process (TMP), different water hardness, and wood supply. Some mills had no scale problem, others experienced different degrees of scaling in specific process areas. To reduce the problem to manageable proportions, we concentrated our efforts on the Millar Western mills. With the support of the management of both Millar Western and National Silicates we adopted a team approach to resolve the scale issues in both mills. The mills are new and use nearly identical equipment and processes. Since both are market pulp mills, they also have more equipment prone to scaling than at an integrated mill.

SCALE CONTROL AT WHITECOURT

Both mills use alkaline peroxide pulping (APP), a variant of the high-yield chemi-thermomechanical process (CTMP) that uses caustic soda rather than sulfite to turn wood chips into pulp. The process consists of three stages of chemical impregnation on wood chips, the third being a bleaching stage, followed by refining, pulp dewatering, and tower bleaching. After souring, the pulp is dewatered on twin-roll presses and then sent to flash drying. The bleaching chemicals include stabilizers-DPTA, magnesium sulfate, and sodium silicate-along with caustic soda and hydrogen peroxide. This article will concentrate on the experience at Whitecourt because that mill experienced several scale problems since startup.

The Meadow Lake mill is a zero-effluent operation using evaporators so scale prevention in the water recovery process has been a priority since the beginning. By controlling the addition rate of magnesium sulfate to sodium silicate, the mill was able to minimize scale formation, especially in the evaporators.

Soon after startup, persistent scale began to form in three major areas at the Whitecourt mill: in the bleach liquor makeup tank, in process piping, and on dewatering presses. The problem was soon persistent enough to shut down some parts of the line for high-pressure cleaning as often as every two weeks. Although silicate is the main chemical component of scale by weight, it is not always the real culprit in the forming of hard, tough scale that clings to steel.

SCALE IN THE SILICATE TANKS AND SUPPLY LINES

Proper handling of sodium silicate is part of our own business, so this problem is the easiest one for us to solve. The silicate was stored hot ($55-65^{\circ}$ C) in the tank using a steam coil. High temperature caused the formation of a crystalline material known as tetrasilicate that would eventually plug the lines and form a large deposit know as a tank bottom. Maintenance crews used steam to clean the lines, which caused more tetrasilicate to form in the lines and further restricted flow. Taking the steam heat out of the tank solved the first problem. Cleaning the lines with warm, dilute caustic soda solved the second problem. Another cause of tank bottoms was the occasional addition of hard water into the silicate tank. Because hard water in the tank forms insoluble calcium silicate, the practice of adding hard water to the silicate tank was stopped.

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SCALE RESEARCH: CALCIUM AND SILICATE COMBINE TO FORM SCALE

To better understand how scaling problems occur, we will review the role of sodium silicate in peroxide bleaching and the conditions that promote scale formation. Sodium silicate stabilized peroxide in mechanical pulp brightening by neutralizing metals that decompose peroxide and reduce its bleaching strength. Silicate is also an alkali source and a buffering agent.

Scale occurs when silicate begins to polymerize, forming larger molecules that eventually drop out of solution and stick to metal surfaces. Under alkaline conditions silicate is stable; however, an acidic pH shock can destabilize the silicate. Calcium or magnesium ions will combine with the silicate polymer to form calcium or magnesium precipitates with a large ratio of silica:calcium or silica:magnesium. Scale is most likely to occur in bleach liquor makeup systems, bleach liquor feed lines, refiners, and bleached pulp dewatering presses. Not coincidentally, the problem areas are the feed and downstream of the hydrogen peroxide addition, which is acidic, or souring acid added after bleaching.

An in-depth study of the interactions of calcium, magnesium, and silicate in peroxide brightening showed that silicate prefers to react with magnesium when both calcium and magnesium ions are present. The resulting magnesium silicates are soft, talc-like precipitates. Magnesium silicate will not stick to stainless: calcium silicate forms scale on steel.

MILL MAGIC FROM MAGNESIUM

Moving to the mill, the results of our research show that by increasing the ratio of magnesium:calcium by addition of a magnesium salt, calcium scale on process equipment can be reduced or eliminated. The next question was: How much magnesium salt (Epsom salt) would be needed to cure scale problems? Our tests showed that a magnesium to calcium ratio of 2:1 or higher was enough to prevent tenacious calcium silicate scale.

Calcium and magnesium have such an important role in silicate scale formation that bleaching operations using high-calcium-hardness process water tend to have more scale problems than operations using soft water. Epsom salt is already applied in mills using peroxide bleaching to preserve bleach liquor and as a peroxide stablizier alone or in combination with silicate during bleaching. In combination, Epsom salt and sodium silicate prevent “glassing” of refiner plates in mills using peroxide refiner bleaching. Finding the correct ratio of calcium:magnesium helped to resolve scale problems at Whitecourt.

SCALE IN BLEACH LIQUOR MAKEUP TANKS AND PIPING

When the Whitecourt mill opened, bleach liquor was prepared as follows. A solution of magnesium sulfate, sodium silicate, and water was mixed in the base liquor tank, followed by separate addition of caustic then hydrogen peroxide downstream in the bleach liquor line. The bleach liquor was then added to the pulp process either in a chip impregnator or to the pulp prior to a bleach tower. Several problems ensued.

Magnesium silicate was precipitating in the base liquor tank and associated piping, causing a loss of base liquor flow. Flow restrictions were measurable

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within two weeks after each pressure cleaning. One proposed solution was to reduce the concentrations of magnesium sulfate and sodium silicate in the base liquor. But the increased volume of base liquor would have required expensive pump upgrades. Instead, a portion of the caustic soda customarily added downstream from the base liquor tank was added directly to the tank. In this way, the silicate in more-alkaline conditions was less prone to form insoluble magnesium silicate. The line stayed clear and the tank required cleaning only during major shutdowns.

Scale also formed in the pipe downstream from the base liquor tank at the addition point for hydrogen peroxide. The pH shock from adding acidic peroxide formed scale at and downstream from the addition point. The answer was to move the peroxide supply pipe. Peroxide entered the bleach liquor just before mixing with the chips or pulp. The close-in addition point allowed no opportunity for pH shock and eliminated scale formation. Also, direct addition of peroxide to the pulp followed by separate addition of the bleach liquor solved the scale problem.

This year Whitecourt developed a new method of adding bleach liquor to pulp. A dilute solution of magnesium sulfate and peroxide is added to the pulp in the dewatering press discharge conveyor. The alkaline solution of caustic soda and silicate is added separately in the high-consistency chemical mixer just before the bleach tower. The new bleach liquor system eliminates mixing tanks in favor of in-line mixing and prevents scale buildup in the piping.

SCALE IN THE REFINERS

Silicate “glassing” of refiner plates developed especially on the softwood line producing market pulp for use in tissue and towel grades. These hot steel plates are ribbed and grooved in a way almost designed to trap scale. As a result, the refiner plates needed more frequent replacement than standard maintenance changeout. Glassing occurred primarily on the softwood line in late summer and fall. Although a combination of silicate and magnesium sulfate can prevent glassing of refiner plates in peroxide refiner bleaching, calcium silicate still formed as a result of high process-water hardness. The calcium silicate problem was resolved by reducing the silicate feed rate by 20% and increasing the magnesium sulfate feed rate.

SUCCESS ON THE DEWATERING PRESSES

The Thune and twin-roll presses each presented different problems on different lines. The Thune presses on the softwood line began as the bidggest headache in the mill and now have become a showcase of low-maintenance operation. These presses were the most direct beneficiaries of the research in scale formation.

Before 1993 the Thune presses on the softwood line were shut down once or twice each month for cleaning. The scale on the presses was a calcium-rich silicate scale adhering to the press wash baskets and restricting the dewatering capacity of the presses. At this point in the line the sodium silicate-to-magnesium sulfate ratio in the back-end bleach liquor was 14:1. In March of 1993 we doubled the quantity of magnesium sulfate, dropping the silicate to magnesium ratio to 7:1. The results were dramatic. Thune press

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washing interval on the softwood line is now once every six months or less frequently.

Our initial work analyzed the composition of the scale on the presses to determine the scope of the problem. Although scale sampling is still a reliable indicator, pressate analysis has now become the method we use to determine the proper addition of magnesium to control scale. On the Whitecourt softwood line a magnesium-to-calcium ratio of 2:1 in the pressate predicts that only soft magnesium silicate precipitate will form. Pressate is much easier to gather and handle than scale and allows frequent, convenient appraisal.

In contrast to the softwood line, Thune presses on the aspen line did not pose a significant maintenance problem. Thune presses on the aspen line are cleaned once every three months, an interval that is within acceptable limits for mill maintenance operations. We have no sure answer as to why scaling is less of a problem on the aspen line. The factors could include lower calcium content of aspen wood and both higher alkalinity and 25% lower silicate addition levels on the aspen line. These factors, alone or in combination, would predict less scale formation.

The twin-roll presses had scale problems that mirrored the Thune presses on each line. The softwood line had more scaling and showed more improvement when more magnesium was added to the back-end bleach liquor. The aspen line had a less-urgent scaling problem.

CONCLUSION: KEEPING SCALE AT BAY

Chemical makeup is the first area to find and fix scaling problems. Dilute the caustic soda in the first cascade tank, then add silicate in the second tank. With caustic thoroughly mixed in the first vessel, hydroxides of calcium and magnesium will form before the addition of silicate. In this way, the metals will be neutralized before they are mixed with silicate, and no scale will form.

Next, add hydrogen peroxide directly to the chips or to the pulp whenever possible. Putting peroxide in the cascade tanks drops the alkaline silicate liquor pH, making conditions right for scale formation. If peroxide must be added to the bleach liquor before the bleaching tower, make the addition point as close as possible to the pulp. Otherwise pH shock will cause scale to form at the peroxide insertion point and downstream in the bleach liquor line. Locating the peroxide addition point in or close to the pulp will not give scale an opportunity to form. Magnesium sulfate should be added directly to the pulp before the addition of the bleach liquor.

Pulp dewatering equipment is a scale-control problem unique to market pulp operations. To keep presses pristine, dilute souring acid with process water or whitewater before combining it with bleached pulp. Dilute acid will cause less pH shock and will form less scale. Since some scale will form as a result of souring, a high ratio of magnesium:calcium before pressing will mean the precipitate that forms is soft, talc-like magnesium silicate. Magnesium silicate does not bind with steel and is easily removed.

Sodium silicate extends the useful life of hydrogen peroxide in pulp bleaching by locking up and neutralizing metal ions in the pulp. Silicate is also an alkali source and a buffer. These documented benefits are indispensable in most peroxide bleaching operations, but maintenance costs can cast a shadow on this necessary chemical. Through careful attention to mixing and addition points of pulping chemicals and additives, silicate scale can be reduced and nearly eliminated. Each mill will differ, but the experience at the Millar Western mill at Whitecourt, AB, shows how scale can be reduced or eliminated through inexpensive and easily duplicated changes to the pulp bleaching and dewatering processes.

WHY SILICATE MERITS SO MUCH ATTENTION

As more and more mills add peroxide to their bleaching sequences and use high-yield pulping methods, sodium silicate will become more common and more important in the chemical mix that mills use to extend peroxide life and effectiveness. The following excerpt from the recently published Pulp Bleaching: Principles and Practices[1] explains the several uses of sodium silicate in peroxide bleaching sequences.

"Several theories about the role of silicate in peroxide bleaching of (chemi-) themomechanical pulp have been suggested. These roles include silicate acting as a peroxide stabilizer, metal ion sequestrant, buffering agent, and metal surface passivator.

…Experience has also shown that, even with the inclusion of pretreatment to eliminate some of the metals [that deactivate peroxide], the addition of silicate in bleach liquor leads to a higher brightness for the same peroxide application…

Peroxide residual is also increased by silicate addition, suggestion that peroxide decomposition is reduced, probably through metal control….

The inclusion of silicate also allows some types of mild steel equipment in peroxide bleaching. Mild steel is not normally used in peroxide service….Silicate, however, coats equipment surfaces, presenting a nonreacting surface for the alkaline peroxide bleach liquor to contact. This allows safe and efficient use of mild-steel equipment such as stock mixers and pumps.

1 Dence, C.W & Reeve, D.W., Eds., Pulp Bleaching: Principles and Practices, TAPPI PRESS, 1996, Atlanta, p. 467.

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