Refiner bleaching with magnesium hydroxide ($Mg(OH)_2$) and hydrogen peroxide

RAY HARRISON, TONY PARRISH, AILEEN GIBSON, CHRIS KNAPP, MARK WAJER, AND DONNA JOHNSON

ABSTRACT: Conventional bleaching of mechanical pulp with magnesium hydroxide and hydrogen peroxide shows significant economic benefits over bleaching with caustic soda and sodium silicate. Magnesium hydroxide [$Mg(OH)_2$] bleaching generates lower effluent BOD/COD, higher pulp yield, lower anionic trash in the paper machines, reduced oxalate scaling and, in some cases, higher bulk.

NORPAC has developed this bleaching process into a commercial, patented refiner bleaching technology. The excellent mixing, high temperature, and high consistency of the refining environment solubilize the magnesium hydroxide and provide an excellent bleach reactor with the addition of hydrogen peroxide. We have shown that by adding magnesium hydroxide into the refining system, refiner energy demand is reduced by 100-200 KW-hr/odmt and pulp strength is improved by 5-10%. In this paper, we describe NORPAC's development of refiner bleaching, University of Maine lab refiner studies that support NORPAC's work, and the additional benefits this technology provides to the mill.

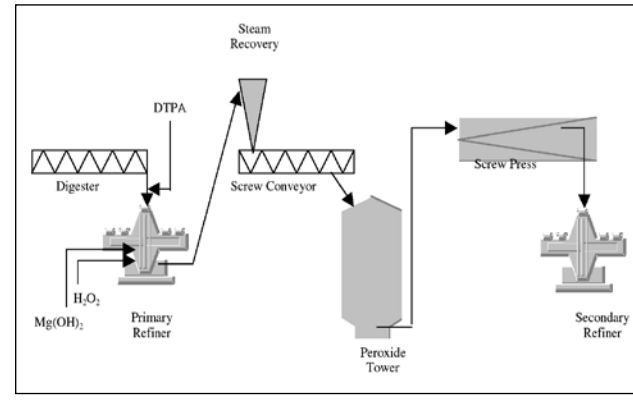
Application: This technology can provide mills with a more efficient peroxide bleach process by adding hydrogen peroxide and magnesium hydroxide in the refining system.

BACKGROUND

North Pacific Paper Corporation (NORPAC), a newsprint mill in Longview, Washington, began investigating alternative alkalis for the bleaching of mechanical pulp in 1999. The initial impetus for considering a different alkali source was driven by a severe calcium oxalate deposition problem that developed when the mill converted to neutral papermaking. Later, the supply and cost variability of NaOH added emphasis to pursuing an alternate alkali source. After several lab and pilot plant studies, $Mg(OH)_2$ was chosen as the most viable alternative alkali from cost, supply and operating simplicity standpoints. We describe the development of refiner bleaching technology, the mill's trial experiences, further lab research and why benefits were achieved in this paper.

The NORPAC TMP mill has a patented inter-stage, alkaline peroxide bleaching process that was converted to $Mg(OH)_2$ in 2004. Two TMP mills contain a total of nine two-stage double-disc refiners, with a peak production capacity of more than 1,500 ODMT/day. Brightness ranges from 52 to 72 ISO, depending on the grade. Three newsprint machines average more than 2,000 swt/day of newsprint and groundwood specialty communication papers.

Figure 1 depicts a simplified process flow. After washing, chips are fed to pressurized digesters for pre-steaming at 45 psig for 2½ minutes. The chips are then treated with DTPA before being fed to the pressurized refiner along with dilution water. The bleach chemicals, $Mg(OH)_2$ and hydrogen peroxide, are also added into the refiner eye. Pulp exits the pressurized refiner into the steam recovery system via a blow line. After steam recovery, a screw conveyor feeds the pulp to a high-consistency bleaching tower for 45 minutes of retention time. The pulp is then re-diluted down to 5% consistency and then thickened to 30% consistency with screw presses just prior to atmospheric secondary refining.



1. NORPAC's process flow.

The NORPAC mill has implemented a patented process for bleaching thermo-mechanical pulp at high temperature and high consistency. Hydrogen peroxide at 40% concentration is pumped directly to the primary refiners. Diethylenetriamine pentaacetic acid sodium salt (DTPA) at a 5% solution concentration is added to the chip feed to the primary refiners. An aqueous, synthetic grade 61% $Mg(OH)_2$ slurry provided by Martin Marietta Magnesia Specialties is added directly to the primary refiners. **Table 1** shows specifications.

MILL TRIALS

We conducted several lab and pilot plant trials before the mill was permanently converted over to $Mg(OH)_2$. The lab and pilot plant data indicated that peroxide bleaching with $Mg(OH)_2$ could provide significant environmental and operational benefits to the mill, including:

1) Reduction of BOD and COD by 20% - 30%, along with a projected yield improvement of 2% - 3%.

Dry Solids Basis	Typical	Specification
$Mg(OH)_2$ purity, %	98.8	98.6 min
Fe, %	0.07	0.10 max
Mn, ppm	100	120 max
Cu, ppm	1	10 max
Median Particle Size, microns	3	---

I. $Mg(OH)_2$ specifications.

2) Energy reduction of 10% due to adding the alkali into the refiner.
3) Bleach cost reduction.
4) Potential to eliminate calcium oxalate deposition.

Encouraged by the lab and pilot plant studies, mill trials were run from early 2001 thru 2003. The initial short term trials were performed using tote bins and peristaltic tube pumps to deliver the $Mg(OH)_2$ to the refiners. The duration of the trials ranged from a few days to six weeks. The short term trials confirmed that 100% of the NaOH and Na_2O/SiO_2 could be replaced with $Mg(OH)_2$ while maintaining the same bleaching response. The mill also found that overdosing $Mg(OH)_2$ created no significant operating issues either in bleaching or refining, as opposed to NaOH, where overdosing would revert the pulp brightness and affect the stability of the refiner operation. Also it was concluded that less alkali dosage was needed with $Mg(OH)_2$ than with NaOH to get an equivalent brightness response.

Although the short term trials were promising, a longer term trial (six months) evaluation was needed to examine all of the impacts to the mill operation. In February of 2003, the mill installed a temporary $Mg(OH)_2$ storage tank (provided by the $Mg(OH)_2$ supplier) to allow for tanker truck deliveries. NORPAC has two TMP mills. The long term trial using $Mg(OH)_2$ as the alkali was done on #2 TMP, leaving #1 TMP on $NaOH/Na_2SiO_3$ bleaching for comparative purposes.

Key findings from the long term trial

- There was no reduction in pulp strength when comparing #1 TMP vs. #2 TMP at the same CSF levels.
- Refining energy was reduced by 100 to 150 kW-hrs/MT.
- Calcium oxalate deposits were eliminated, allowing the scale inhibitor to be removed.
- Retention aid chemistry on the paper machines was changed due to the reduction in anionic trash from TMP.
- Peak brightness capability was maintained with $Mg(OH)_2$ as the alkali.
- There was a reduction in BOD/COD in effluent that directly correlated with the conversion to $Mg(OH)_2$.
- A 1% overall TMP yield improvement resulted even though only half the TMP production was converted to $Mg(OH)_2$.
- Bleach cost savings alone could justify capital expenditure of a permanent $Mg(OH)_2$ storage and delivery system, with a payback of less than six months.

The mill approved a permanent $Mg(OH)_2$ system in June of 2003. The #2 TMP system was started up in December of 2003, with the #1 TMP system starting up in February 2004. The system has been running successfully with 100% uptime to date. A modification in July 2004 that introduced hydrogen peroxide directly into the refiner, rather than in the downstream blow line, improved bleaching efficiency by more than 10%, due to improved mixing and increased bleaching consistency. U.S. patents on the bleaching process were issued in June 2004 and April 2005. A Canadian patent on the process was issued in January 2005.

RESULTS AND DISCUSSION

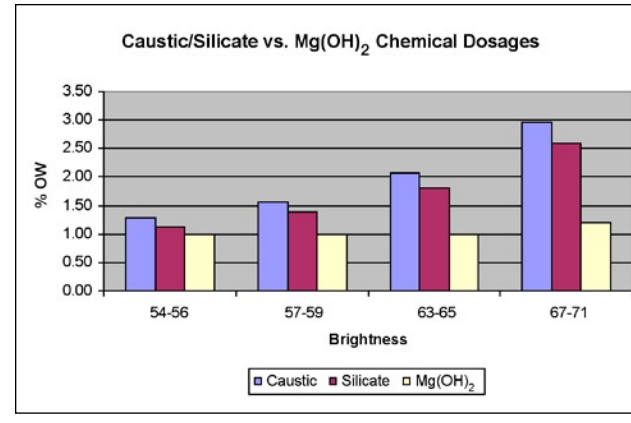
Bleaching Cost

The reduction in bleach costs using $Mg(OH)_2$ as the alkali source is achieved for two fundamental reasons:

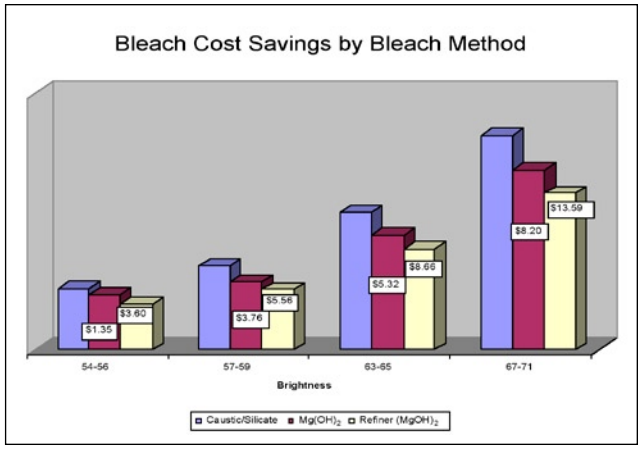
1) Peroxide stabilization and the pH buffering provided when $Mg(OH)_2$ is the alkali source allow sodium silicate to be removed without affecting bleach efficiency. This reaction is described by Nyström et. al. [1].
2) The number of acidic groups generated during bleaching determines the demand for $Mg(OH)_2$. In most cases, as long as the pH is above 7.0, a lesser amount of $Mg(OH)_2$ is sufficient.

Consequently, there is a savings potential, and the alkalinity demand for caustic soda is higher than for $Mg(OH)_2$. This is reported by Seuss et. al. [2] and is confirmed with mill results. As the brightness is increased, the caustic/silicate must be increased along with peroxide. Magnesium hydroxide, however, remains constant at 1% OW (on wood) with increasing peroxide dosages and is raised only to 1.2% OW to reach peak brightness capability, as demonstrated in **Fig. 2**.

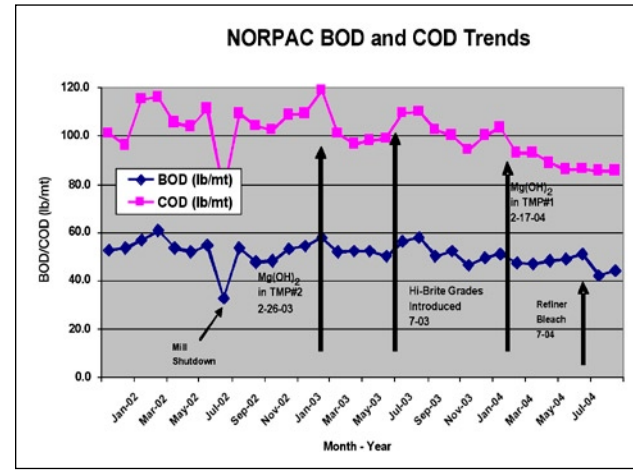
Figure 3 shows the bleach cost savings on a per-ton basis. The savings vary by brightness target and use the caustic/silicate bleaching as the base case for comparison. The $Mg(OH)_2$ case shows the savings with $Mg(OH)_2$ added to the refiner and hydrogen peroxide added downstream in the blow line. The refiner $Mg(OH)_2$ case displays the savings the mill experienced when $Mg(OH)_2$ and hydrogen peroxide are both added in the refiner. The additional savings are due to improved bleach re-



2. Alkali dosages for various brightness targets.



3. Comparison of bleach cost savings by bleach method.



5. Organic loading in NORPAC's bleach effluent.

sponse due to improved mixing of chips and bleaching chemicals and a higher consistency, which result in a lower peroxide dosage to achieve the same final brightness target.

Refining energy

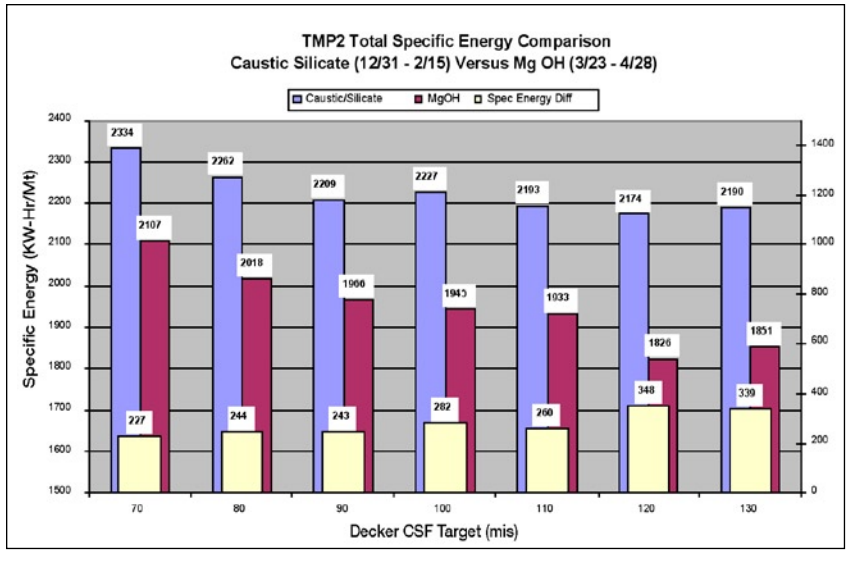
The fiber swelling and loosening of the lignin bonds when an alkali source is added during or prior to refining has a significant effect on refiner specific energy consumption. This is documented by Kappel [3]. **Fig. 4** shows the energy reduction by freeness target when $Mg(OH)_2$ was applied directly into the refiner versus the mill's previous process configuration where caustic and silicate were added downstream of the primary refiner in the blow line.

BOD & COD

Typically in mechanical pulping, COD/BOD is generated from the defiberization and bleaching processes. In the case of peroxide bleaching with caustic soda, as the brightness target increases the caustic application is increased resulting in higher COD/BOD loads. When using $Mg(OH)_2$ as the alkali source, the relationship between alkalinity and the bleach reaction changes (as seen in Fig. 2). The lower alkalinity needed to achieve the bleach response with $Mg(OH)_2$ helps reduce COD/BOD loading. The low solubility and alkalinity provided by the divalent base $Mg(OH)_2$ is another factor that lowers COD/BOD loading. The reduction in COD/BOD loading using $Mg(OH)_2$ versus caustic soda is well documented in literature [2] [4] [5], and generally confirms a reduction of between 20% to 40%. Mill data show a significant reduction in BOD/COD with the conversion to $Mg(OH)_2$ as seen in **Fig. 5**. From the mill data, it is obvious that there were step changes when #2 TMP was converted to $Mg(OH)_2$ and again a year later when #1 TMP was converted to $Mg(OH)_2$.

Yield

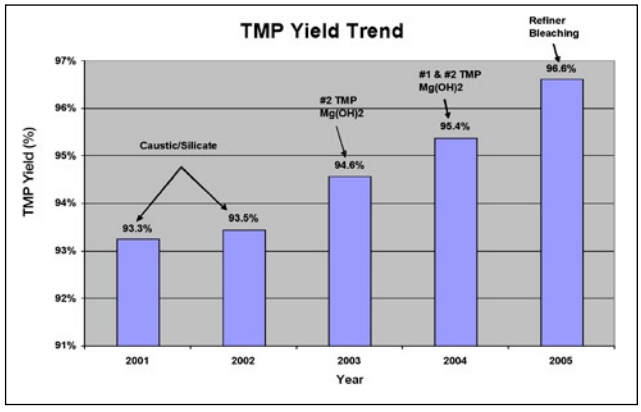
Peroxide bleaching of mechanical pulps can reduce yield from 2% to 5% depending on bleach conditions and wood species. Using $Mg(OH)_2$ causes less dissolution of the pulp than caustic soda, resulting not only in lower COD/BOD but in increased pulp yield. A typical TMP yield for the mill with caustic soda as the alkali source for bleaching was 93.5%, shown in **Fig. 6** for the years 2001 and 2002. When #2 TMP was converted to $Mg(OH)_2$ in 2003, the TMP yield increased by 1%. With the conversion of the other TMP to $Mg(OH)_2$ in 2004, the yield increase was 2% over the caustic/silicate base case. In 2005 when peroxide was added to the refiner bleaching, efficiency improved by more than 10%, and another 1.0% yield improvement was achieved.



4. Comparison of refiner energy by bleach method.

Calcium oxalate

The initial impetus for the mill to investigate an alternative alkali was excessive calcium oxalate deposits as a result of converting the mill to neutral paper making. Peroxide bleaching is the major source of oxalate generation in the mill and necessitated the need for a costly scale inhibitor program to prevent calcium oxalate scale



6. TMP yield by bleach method.

deposits in pipes and on machine surfaces. The formation of oxalate from the $Mg(OH)_2$ peroxide bleaching was investigated by L. Yu, M. Rae and Y. Ni [6]. They concluded that the $Mg(OH)_2$ bleached pulp generated the same amount of oxalate as the caustic soda bleached pulp. The difference is that the $Mg(OH)_2$ bleached pulp forms oxalate in a soluble state, as opposed to the caustic soda bleached pulp in which a large portion of the oxalate generated is in precipitate form. Thus the $Mg(OH)_2$ bleached pulp significantly reduces or eliminates oxalate-related scaling issues. The impact of $Mg(OH)_2$ bleaching on calcium oxalate scale was clearly observed in the TMP mill. Bleaching with caustic soda, the mill used a scale inhibitor and still had scale deposits that had to be removed physically with pressure washing. Once the mill was fully converted to $Mg(OH)_2$ bleaching, the scaling issues were reduced to the point where the scale inhibitor was removed and cleanup of piping and equipment due to oxalate scale deposits was eliminated.

Ease of operation

Previous attempts to bleach in the refiner met with varying success. There have been two major drawbacks with silicate/caustic soda-based bleaching: 1) silicate scaling causing the refiner plates to fill in; and 2) caustic soda can affect the viscosity of the pulp resulting in unstable refiner loading. The mill has had no issues with plate filling or impacts to refiner stability since the conversion to $Mg(OH)_2$. The $Mg(OH)_2$ refiner bleaching process couples refining with bleaching, thus taking full advantage of the alkaline environment to improve fiber development and decrease specific energy.

Bleach variability has been greatly reduced with $Mg(OH)_2$. The caustic/silicate system must be monitored continuously to ensure that the caustic application is not too low, creating high peroxide residuals and low bleach efficiency, or too high, where peroxide residual is totally consumed and brightness reversion occurs. With the $Mg(OH)_2$ system, peroxide is dosed to achieve a given brightness target, and due to the buffering nature of $Mg(OH)_2$, it can be applied at a 1% OW or lower dosage regardless of the brightness target. If overdosing of $Mg(OH)_2$, occurs, there is virtually no impact on bleach response. Using the refiner as the bleach mixer allows the bleaching chemicals to be applied neat, thus eliminating the need for chemical make down systems.

FURTHER LAB STUDIES

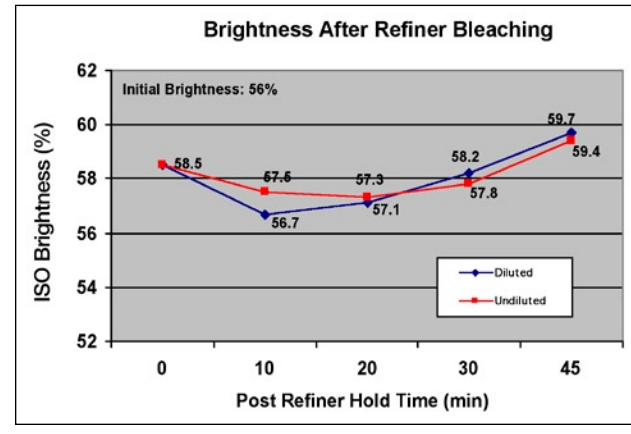
Since conventional refiner systems do not incorporate an interstage bleach tower to allow additional time for the peroxide reaction to occur, we performed laboratory work to determine if an increase in brightness could still be achieved if refiner bleaching is followed by a dilution step (e.g., latency chest).

The University of Maine conducted lab refiner studies using $Mg(OH)_2$ and peroxide to bleach TMP in a refiner system. The pulp sample used in the study was obtained from another TMP mill from the eastern U.S. In the lab, researchers evaluated softwood TMP that was mill refined through primary and secondary refiner systems, bleached with hydrosulfite, and screened. The objective of the study was to determine the feasibility of refiner bleaching with $Mg(OH)_2$ and peroxide in the mill's downstream reject refiner system.

The pulp sample we received measured 360 mL CSF and 28% consistency. We mixed the pulp in a Hobart mixer with bleach liquor consisting of 2% peroxide, 0.75% $Mg(OH)_2$ (see Table I for specifications) and 0.2% DTPA in 500 mL of water. We then processed the pulp mixture through a 12-inch Sprout-Bauer mechanical refiner to a target freeness of 140-150 mL CSF at the refiner discharge. We used whitewater from the mill as dilution water during refining, which resulted in 12% -15% pulp consistency at the refiner discharge.

During the run, we removed pulp samples from the receiving tank of the refiner, bagged, sealed and placed them in a water bath at 80°C. Since the mill's reject refiner is followed by a reject holding tank that dilutes the pulp down to 7% consistency and has a retention time of 45 minutes, the post-refiner bleached pulp was also diluted with white water to 7% - 10% consistency and held in the water bath at various retention times up to 45 minutes. As a comparison, undiluted, post-refiner bleached pulp (12% - 15% csy) was also held in the water bath at the same time intervals.

Figure 7 compares the brightness of the undiluted and diluted refiner bleached pulps. The brightness of the pulp increased immediately after refiner bleaching, with no hold time, from 56% ISO unbleached to 58.5% ISO. At the 10-, 20- and 30-minute intervals however, brightness decreased slightly. At the end of 45 minutes, brightness recovered for both samples, as a



7. Brightness development after lab refiner bleaching.

3+ point brightness gain was achieved after refiner bleaching. The brightness curves for the diluted and undiluted samples were similar, indicating that a low consistency step after refiner bleaching did not greatly affect brightness development. This lab study demonstrated that mills with a conventional refiner system and a latency chest after the refining system can still benefit from refiner bleaching with $Mg(OH)_2$ and peroxide.

CONCLUSIONS

The $Mg(OH)_2$ refiner bleaching system provides significant environmental and process benefits to NORPAC. We have been operating with this bleach method for more than two years and it has proven to be safe, reliable, and simple to operate. The benefits achieved include: 1) reduced bleach costs, 2) lower refiner specific energy, 3) decrease in BOD/COD, 4) increased yield, and 5) elimination of calcium oxalate scaling issues. The technology is adaptable to various refiner configurations and easy to test because of the simplicity of the chemistry and application method. NORPAC has obtained patents [7,8,9] for refiner bleaching with $Mg(OH)_2$ and has licensed the technology to Martin Marietta Magnesia Specialties. **TJ**

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INSIGHTS FROM THE AUTHORS

We chose this topic to research because refiner bleaching with magnesium hydroxide and peroxide appeared to be a viable technology for bleaching chemistry improvement in the TMP mill at NORPAC. The work we did builds on patented interstage bleaching technology developed at NORPAC in the mid-1980s. The modified interstage bleaching chemistry developed at that time resulted in significant cost savings for the mill.

The most difficult problem we encountered at the outset was to get acceptance within the mill for trying the change without knowing its full effects on pulp quality and paper machine operation. We addressed the risk issue by conducting lab trials, then pilot trials and, finally, short mill trials on individual refiners to prove that the chemistry worked. The final proof was a TMP mill trial that evaluated all effects, including paper machine operation and pulp strength evaluations.

The results of our research have been very satisfying. We discovered and proved that significant improvements in mill operations and cost reduction can be achieved with low-cost changes in existing process variables. Basic research can lead to major business improvements.

Other mills can benefit from our research because any TMP mill that bleaches with peroxide can use this patented technology to achieve bleach cost savings. NORPAC has fully implemented this technology, but additional research is underway to make further improvements to the mill's bleaching system.

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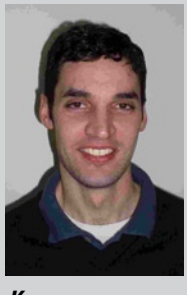
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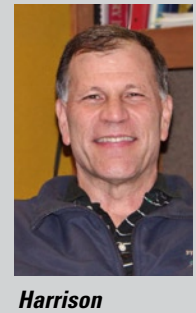
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