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Effects of an Organotitanate Cross-linking Additive on the Processing and Properties of Macro-Defect-Free Cement

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We have investigated the effects of an organotitanate cross-linking additive on the processing and moisture sensitivity of macro-defect-free (MDF) cements. The modified samples were formed by a two-part process: first, the as-received calcium aluminate cement powder was coated with the organotitanate compound, followed by the standard MDF cement fabrication procedure. It was estimated that 6 wt% (by weight of the cement powder) of the additive was adsorbed. Rheological measurements showed that cross-linking reactions between the organotitanate additive and the polymer (polyvinyl alcohol-acetate) used to form MDF cement occurred during the high shear mixing process. This led to a 65% reduction in the processing window for the modified pastes as compared to the standard MDF cement pastes. However, the organotitanate-modified MDF cement samples exhibited improved moisture resistance as compared to the standard samples when exposed to 100% relative humidity at 22°C. The most significant result was that the modified samples retained nearly 100% of their initial strength after 200 days of exposure to these conditions, whereas the strength of the standard MDF samples was decreased by approximately 45%. ADVANCED CEMENT BASED MATERIALS 1995, 2, 2–7

KEY WORDS: Macro-defect-free cement, Moisture resistance, Polymer cross-linking

Macro-defect-free (MDF) cements, developed a decade ago by Birchall et al. [1], have been the subject of several investigations [2–6] and review articles [7,8] due to their superior mechanical properties relative to other cement pastes. Birchall et al. [9] found that optimal properties were obtained when calcium aluminate cement (CAC)[1] was combined with a polyvinyl alcohol-acetate (PVAA)[2] copolymer [10] and a small amount of water to form this material. Early work [11–13], however, revealed that these properties degraded significantly upon exposure to moisture. This discovery served to focus subsequent investigations on (1) understanding the microstructure of MDF cement and its relation to moisture transport and the degradation process [14–17] and (2) improving the moisture resistance of this material [18,19].

Popoola et al. [14] were the first to observe an interphase region, containing both cement hydration products and polymer intimately mixed at the nanometer level, located at the interface between unreacted calcium aluminate cement grains and the polymer matrix in MDF cement. In addition, they demonstrated, through in-situ environmental transmission electron microscopy (TEM) studies [15], that the polymer and interphase regions absorbed moisture when exposed to humidity. Lewis et al. [16] subsequently studied the percolative properties of the bulk polymer and interphase regions, through a combined approach of experiments and computer simulations using the hard core/soft shell continuum percolation model [20]. They determined that although both the bulk polymer and interphase regions form connected pathways through the three-dimensional MDF cement microstructure, the bulk polymer regions served as the main pathway for moisture transport. Their work confirmed earlier hypotheses that the polymer matrix, due to its affinity for water, was primarily responsible for the moisture sensitivity of this system. Hence, it follows that one strategy for improving the moisture resistance of MDF cement is to render those regions containing polymer (i.e., the bulk and interphase regions) insensitive to water.

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Received February 22, 1994; Accepted April 21, 1994

[1] Cement chemistry notation is used: C = CaO, A = Al_2O_3, and H = H_2O. The abbreviation CAC is used to denote calcium aluminate cements which contain other phases in addition to the principal CA phase.

[2] IUPAC recommended notations used [10]: PVAA = partially hydrolyzed polyvinyl alcohol, also referred to as polyvinyl alcohol-acetate copolymer.

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/95/$9.50
SSDI 1065-7355(94)00020-E

In preliminary research by Desai [19], several polymer (PVAA) cross-linking additives were surveyed with respect to their ability to improve the moisture resistance of MDF cement. One promising additive emerged from their research, an organotitanate cross-linking agent (Tyzor TE™; DuPont de Nemours), which merited further investigation. This commercial additive is compatible with the high pH environments generated during fabrication of MDF cement and is well known to cross-link PVAA. Chemically, it is a mixture of various chelates with at least one component in the solution identified to be triethanoalamine titanate chelate [21]. This component has a cage structure as shown in Figure. 1. The cross-linking of PVAA by Tyzor TE is reported to follow the reaction sequence shown in Figure 2, which can be initiated above 100°C or in high pH (pH 6 to 10) environments. A recent investigation by Gulgun et al. [22] has shown that a 5 wt% solution of fully hydrolyzed polyvinyl alcohol in water could be gelled at room temperature within seconds upon the addition of this additive. In this article, we report on how the Tyzor TE organotitanate cross-linking additive affects the processing and moisture sensitivity of MDF cements.

Experimental Procedure

Standard MDF cement samples (i.e., without the organotitanate additive) were fabricated using the process developed by Birchall et al. [9] and optimized by Russell [23]. Their starting composition consisted of 150.0 g of calcium aluminate cement (Secar 71; Lafarge International, Chesapeake, VA), 10.5 g of PVAA (Gohsenol KH-17s; Nippon Gohsei, Inc., Osaka, Japan), and 1.05 g of glycerol (a plasticizer for PVAA). The PVAA used had an average molecular weight of 105,000 g/mol and an acetate content of 22%. These individual constituents were first premixed for 210 seconds in a planetary mixer. This was followed by high shear mixing on a twin roll mill, and, finally, calendaring to form sheets whose approximate dimensions were 300 × 150 × 2 mm. Half of these sheets were pressure cured at 80°C and 5 MPa (725 psi) for 600 seconds, followed by a 24 hour cure at 105°C in a drying oven, while the remainder were pressure cured at 105°C and 725 psi for 600 seconds, followed by an identical oven cured process. Cylindrical samples (30 mm in diameter) were core drilled from the as-cured sheets and subjected to further evaluation. A more detailed description of this process is given by Russell et al. [18]. The standard MDF cement samples served as control samples for these experiments.

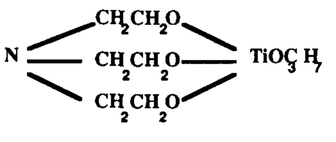

FIGURE 1. Chemical structure of triethanoalamine titanate chelate, a known component of the Tyzor TE cross-linking additive [21].

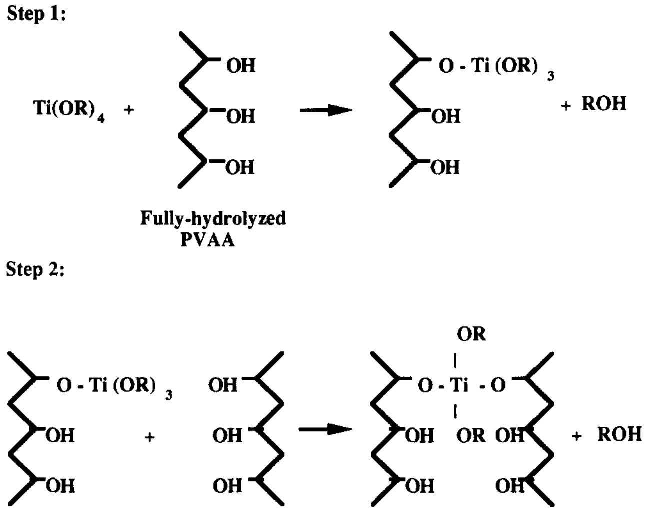

FIGURE 2. Reaction sequence between Tyzor TE additive and fully hydrolyzed polyvinyl alcohol [21]. The PVAA used in this study is 78% hydrolyzed.

Tyzor TE modified MDF cement samples were fabricated by a two-part procedure. In the first part of this procedure, the organotitanate additive was adsorbed onto the surface of the as-received CAC powder. The objective of the coating process was to provide a means of uniformly distributing this additive in the final MDF cement microstructure. In previous work [18,19], such additives were simply added in bulk to the starting batch composition. The coating process was achieved by preparing a solution that contained 150 g of the CAC powder in 1000 ml of isopropyl alcohol (IPA). 15 g of Tyzor TE solution (80 wt% additive and 20 wt% IPA) was added to this solution and it was allowed to stir for 24 hours. The cement powder was then filtered from the solution and dried, leaving behind an agglomerated particulate layer which was easily ground into powder form. A similar procedure (without the introduction of the Tyzor TE solution) was repeated to produce a control sample of the CAC powder. Thermogravimetric analysis (TGA) was then performed on a small amount (≈30 mg) of the control- and as-coated CAC powders to determine the amount of Tyzor TE absorbed. These samples were heated at 5°C/minute in air to 1000°C and their weight loss was measured as a function of temperature. In the second part of this procedure, the as-coated CAC powder was substituted for the CAC powder used in Table 1 and these batches

TABLE 1. Batch composition of MDF cement samples

Component	Weight (g)	Weight (%)	Volume (%)
HAC cement*	150.00	84.25	65.21
PVA‡	10.50	5.90	12.30
Glycerol	1.05	0.58	1.35
Deionized water	16.00	9.27	21.34

*Secar 71; Lafarge Calcium Aluminates, Inc., Chesapeake, VA.
‡Gohsenol KH-17s; Nippon Gohsei, Inc., Osaka, Japan.

were processed by the same procedure described above.

The rheology of both Tyzor TE-modified and standard MDF cement pastes was characterized using a Banbury mixer (Haake Rheocord System 90 and Rheomix 600; Fiscons Instruments, Paramus, NJ). Approximately 40 g of cement paste was placed into a chamber which contained two mixing heads rotating at 100 rpm. The torque response and paste temperature were measured as a function of time. The paste temperature did not exceed 50°C during these measurements. A more detailed description of these measurements can be found in ref 25.

Representative as-cured samples of the Tyzor TE-modified and standard MDF cement were exposed to 100% relative humidity at 22°C. Their weight gain was measured as a function of time during long-term exposure (>100 days). In addition, their initial strength as well as intermittent strengths during moisture exposure were measured by the biaxial flexural method [24]. Selected samples were heated to 500°C at 1°C/minute in air to remove the volatile constituents associated with the binder phase (defined as both the bulk polymer and interphase regions). The resultant pore structure of each sample was characterized by mercury intrusion porosimetry (Micromeritrics Autopore II 9220, Norcross, GA).

Results and Discussion

The TGA results are shown in Figure 3 for both the Tyzor TE-coated and the control CAC powders. The difference in weight loss observed between these samples was used to estimate the amount of the organotitanate additive adsorbed onto the CAC powder surface. To perform this calculation, it was first assumed that the chemical structure of the triethanoalamine titanate chelate (refer to Figure 1) was representative of the majority of the chemical species present in Tyzor TE. Secondly, it was assumed that upon heating to 1000°C in air, this compound decomposed to TiO_2. From the measured weight loss difference between these samples, it was found that 5.9 wt% Tyzor TE was adsorbed onto the surface of the CAC powder. This value is an approximate one given these assumptions.

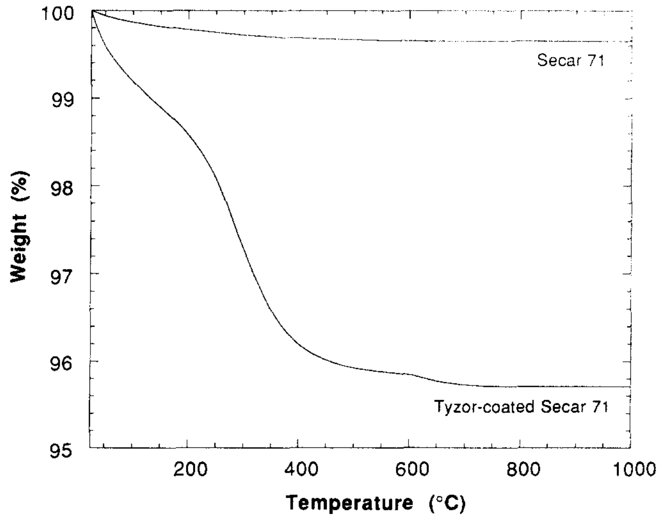

FIGURE 3. TGA of the Tyzor TE-coated and the control CAC powders heated to 1000°C at 5°C/minute in air.

Figure 4 shows the rheological behavior of both standard and Tyzor TE-modified MDF cement pastes, where torque is plotted as a function of time. To aid our interpretation of these results, we have compared our observations to those reported by McHugh and Tan [25]. They have studied the complex rheological behavior of standard MDF cement paste (same composition) in greater detail. They attributed the gradual rise in the torque with time to the second torque maxima (plateau region) to the development of a cross-linked network within the paste resulting from reactions between cement hydration products and PVAA.

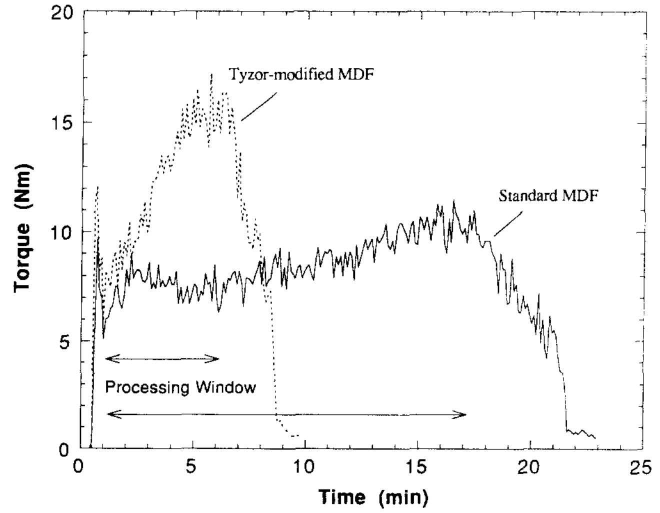

FIGURE 4. The rheological behavior given by torque as a function of time for the Tyzor TE-modified and standard MDF cement pastes. Top and bottom arrows represent the processing windows of the modified and standard systems, respectively.

Beyond the plateau region, the torque was observed to rapidly decrease as the cement paste broke down into a friable mass. An important contribution of their work was the definition of a "processing window," extending from the initial measurement of torque to the second torque maxima, which can be used to compare the effects of different compositions and properties on the processing of MDF cement pastes.

The basic features of the torque-time response for both the standard and Tyzor TE-modified MDF cement pastes (refer to Figure 4) are analogous to those reported earlier [25]. A processing window of 17 minutes was observed (refer to Figure 4) for the standard MDF cement, which is in good agreement with previous observations [25]. In contrast, the Tyzor TE-modified cement paste had a much narrower processing window of approximately 6 minutes. In addition, the torque curve for the modified system displayed a sharper rise to the second torque maxima compared to the standard MDF cement paste. These observations suggest that the organotitanate additive is accelerating the development of a cross-linked paste network (refer to Figure 2). This is consistent with the observations reported by Gulgun et al. [22] discussed earlier. Yet, there appears to be a difference in the kinetics of cross-linked formation between the pastes studied here and the polymer solutions investigated in their work, which permits these systems to be fabricated into MDF cement. The sharp reduction in processing time for the Tyzor TE-modified cement pastes has important ramifications for its final microstructure. If the material is overprocessed during fabrication, voids (macro-defects) can be reintroduced into the paste, resulting in degraded mechanical properties [25].

It is noteworthy that the MDF cement pastes containing a similar amount of the organotitanate added in bulk (as described by refs 18 and 19), rather than the two-part process, displayed intermediate rheological behavior as compared to the modified and standard MDF pastes reported here [26]. Both the slope of the torque curve between the first and second torque peaks, as well as the processing window (≈12 minutes), lie between those observed in our systems. The primary difference between these two modified MDF cement pastes is the initial distribution of the organotitanate additive. While a more homogeneous distribution of Tyzor TE leads to reduced processability, we found that this approach yields a material with enhanced moisture resistance [26].

Figure 5 shows the weight gain as a function of time for MDF cement samples exposed to 100% relative humidity. For comparison, the weight gain of standard MDF cement is also included. The Tyzor TE-modified MDF cement samples cured at 80°C/105°C and 105°C/105°C (pressure cure/oven cure) exhibited improved moisture resistance over the standard MDF cement samples cured under the same conditions, respectively. The greatest improvement was observed for the Tyzor TE samples cured at 80°C/105°C, which showed approximately 35% less weight gain than the analogous standard samples. While it is unclear whether further cross-linking of PVAA by the organotitanate additive occurred during the curing process at temperatures above 100°C [21], our results suggest that the initiation of such reactions during the oven curing process (in a pressure-free environment) may be preferable.

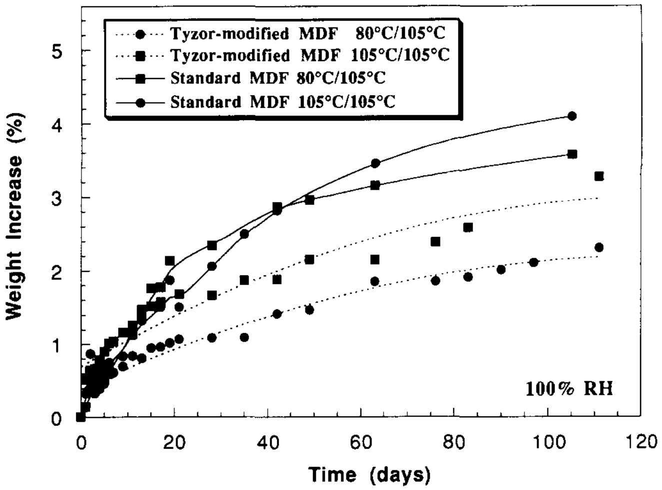

FIGURE 5. A plot of weight gain as a function of time for the Tyzor TE-modified and standard MDF cement samples exposed to 100% relative humidity.

The normalized flexural strength as a function of time for the Tyzor TE-modified and standard MDF samples exposed to 100% relative humidity is shown in Figure 6. While initial flexural strengths of the Tyzor TE-modified MDF cement samples were lower than the standard MDF samples processed under identical conditions, their resistance to strength degradation was greatly improved (refer to Figure 6). For example, the Tyzor TE-modified MDF samples cured at 80°C/105°C and 105°C/105°C had initial strengths of 165 and 140 MPa, respectively, and after exposure to moisture for 200 days their strengths were 155 and 145 MPa, respectively. Conversely, the initial strengths of the standard MDF samples are 190 to 215 MPa, respectively; however, after exposure to moisture for 200 days, their strengths decreased to 100 to 130 MPa, respectively. The most significant feature of these results is that the modified MDF cement samples retained their initial strength properties while being exposed to 100% relative humidity for a period of 200 days. This result combined with the lower weight gains exhibited by the organotitanate-modified samples supports the conclusion that the addition of Tyzor TE improves the moisture resistance of MDF cement.

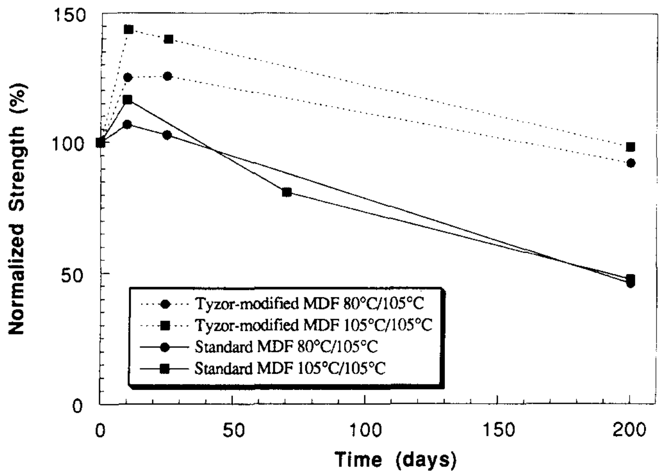

FIGURE 6. A plot of the normalized flexural strength (calculated as the observed strength divided by the initial strength ×100%, where each data point reflects an average value obtained from five samples) as a function of time for the Tyzor TE-modified and standard MDF cement samples.

A possible explanation for the lower initial strengths of the organotitanate-modified samples relative to the standard MDF cement samples is that similar processing times were used during their high shear mixing and calendering steps. As discussed previously, these steps have been optimized [23] solely for the standard MDF cement samples. Thus, it is likely that using these same conditions for the modified-MDF cement samples would produce an overprocessed system given their markedly different processing windows (refer to Figure 4). A negative result of overprocessing is the reintroduction of large voids within the paste, as demonstrated by McHugh and Tan [25], which naturally would yield lower strength materials. Hence, we probed the resulting pore structure of the binder-free samples by mercury intrusion porosimetry to determine whether there were differences in large-scale pore content (defined as pore diameters >0.1 μm) between these samples.

Figure 7a and b shows the MIP results plotted as cumulative volume of mercury intruded versus pore diameter for heat-treated Tyzor TE-modified and standard MDF cement samples cured at 80°C/105°C and 105°C/105°C, respectively. The general features of each of these curves are in good agreement. However, there is one notable difference. The Tyzor TE-modified samples showed greater cumulative intrusion of mercury in the larger pore diameter (D_{pore}) range (defined as $D_{pore} > 0.2$ μm). This is particularly apparent for the MDF samples cured at 105°C/105°C. This observation supports the hypothesis that the Tyzor TE-modified samples were slightly overprocessed, leading to a larger pore structure. Given the overall similarity between the pore-size distributions of these samples ($D_{pore} \leq 0.2$ μm), it appears that the addition of Tyzor TE will not negatively impact microstructural development of those MDF cement pastes once their processing is fully optimized.

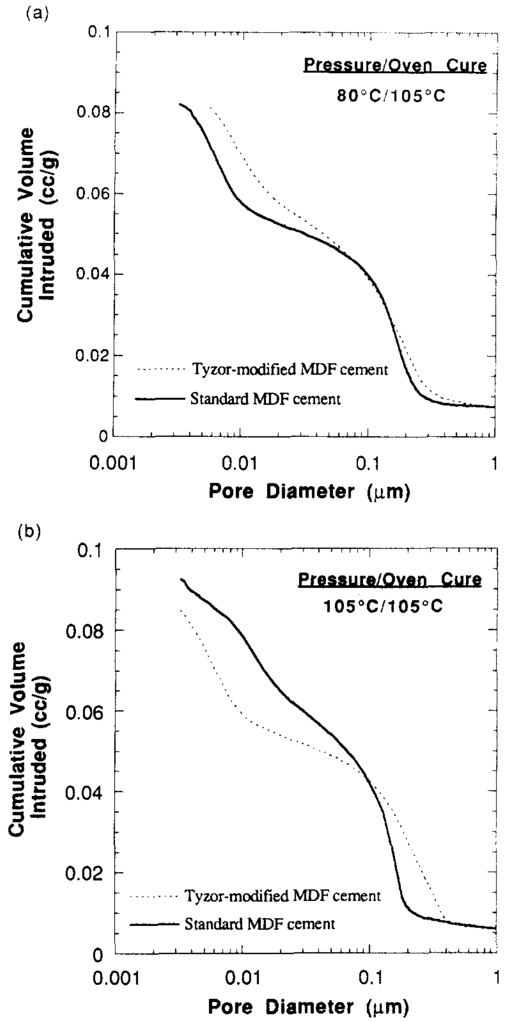

FIGURE 7. Mercury intrusion porosimetry results, plotted as cumulative volume of mercury intruded versus pore diameter for heat-treated Tyzor TE-modified and standard MDF cement samples. (a) Samples cured at 80°C/105°C (pressure cure/oven cure) and (b) samples cured at 105°C/105°C.

Conclusions

MDF cements have commercial potential in several technological areas, provided their moisture sensitivity problems can be successfully addressed. In this work, we have demonstrated that the moisture resistance of MDF cements can be improved through chemical modification of the polymeric regions within their microstructure. Specifically, the effects of an organotitanate cross-linking additive on the processing and moisture sensitivity of MDF cements were studied. We showed that a significant improvement in both moisture absorption and resistance to strength degradation in a 100% relative humidity environment was achieved in the organotitanate-modified MDF cement materials. However, a key limitation of this specific cross-linking additive was that partial initiation of these reactions with the polymer (PVAA) phase occurred during the high shear mixing process. This led to a reduced processing window, and yielded components of lower initial strength relative to the unmodified (standard) MDF cements.

In summary, our observations provide guidelines for future studies on the effects of chemical modifiers on MDF cements. While our research suggests that cross-linking the polymer phase is a promising approach to minimizing the moisture sensitivity of this system, Tyzor TE was not an ideal additive due to its chemical reactivity with PVAA under ambient conditions. The optimal cross-linking additive would possess the ability to strongly bond the polymer chains together, but not be chemically activated until the curing process. This would allow the MDF cement pastes to be formed into complex shapes (e.g., through extrusion or injection molding techniques) without increasing the likelihood of reintroducing macro-defects due to overprocessing.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the NSF Science and Technology Center for Advanced Cement Based Materials under grant No. DMR 91-2002. We would also like to thank Professors J.F. Young, A. McHugh, and M. Berg for their helpful insights into this work.

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