

Varying electro-kinetic interactions to achieve predictable removal rates and smooth surfaces on ZnS

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ABSTRACT

A conventional polishing study was conducted with infrared material zinc sulfide with the goal of producing defect-free polished surfaces in *predictable* amounts of time. Utilizing the measured electro-kinetic properties of the zinc sulfide and polishing abrasives, polishing slurries were selectively altered and the resulting removal rates and surface roughness values were measured. This paper will serve as a baseline for developing an empirical model for optimizing both surface roughness and removal rate for two different types of abrasives and two pitch types with ZnS.

Keywords: Zinc sulfide, polishing, infrared materials

1. INTRODUCTION

The application of zinc sulfide (ZnS) and zinc selenide (ZnSe) to the field of optics dates back to the 1950's.¹ Zinc sulfide produced by chemical vapor deposition results in a cubic, polycrystalline material that transmits in the infrared region. There are typically two types of ZnS, standard grade and multispectral ZnS.² Over the past thirty years, a few have published polishing recipes for working with ZnS and ZnSe materials and many optical shops have developed their own internal standard process, but still today as new opticians enter the scene many struggle with this material upon their first exposure.³⁻⁵

Chemo-mechanical interactions between optical glass and polishing abrasives has previously been discussed by both Cook⁶ and Cumbo⁷. Cook⁶ analyzed previously published data for oxide polishing abrasives and optical glasses and developed an equation for polishing rate which was dependent upon the (polishing abrasive) oxide single bond strength (sbs), the polishing abrasive slurry pH and the isoelectric point (IEP). [The IEP is the slurry pH where there is no net surface charge on an oxide (substrate or abrasive).] Cook stated that the polishing abrasives should have IEP values similar to the slurry pH, and that the slurry pH should have a higher pH than the glass surface in order to maximize removal rates. The optimum pH for CeO₂ and ZrO₂ working silicate glasses was hypothesized to be 9.8.

Cumbo et al.⁸ were also interested in achieving the smoothest surfaces for silicate glasses, unlike Cook who was interested in predicting the conditions for maximum removal. Cumbo developed the slurry-charge-control effect that states that, for silicate glass types, the abrasive IEP should be lower than the pH of the fluid. This resulted in the same sign for the surface charges on the glass and the polishing agent. Cumbo found that this condition produced the smoothest surfaces, because surface chemistry prevented particle agglomeration. He found that when the mean particle size (due to agglomeration) was larger, the rms surface roughness was higher. Consequently, this situation also yielded high removal rates for certain abrasive/glass combinations, because minimal agglomeration of slurry particles was thought to promote better fit to the lap and closer contact of more abrasive particles to the part surface.

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2. ELECTRO-KINETIC PROPERTIES

Zeta potential is the charge a particle acquires under flow within in a particular medium. The zeta potential of the particle is the potential measured at the slipping plane (see Figure 1) in a suspension. A negatively charged particle will attract positively charged ions that are present in a suspension. Ions that are strongly bound to the particle form the Stern layer. Ions that are less firmly attached, but still move or travel with the negatively charged particle, form a diffuse region. The boundary of this diffuse region is referred to as the slipping plane.⁹

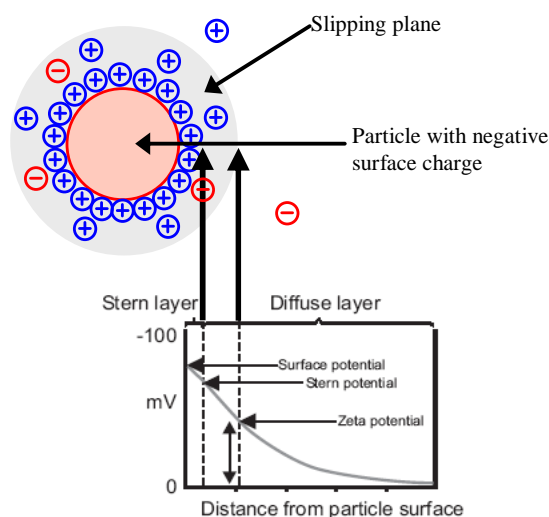


Figure 1: Drawing of a negatively charged particle in suspension. [Adapted from Ref. 9].

The magnitude of the zeta potential is a strong indication of the stability of the colloid suspension. If the zeta potential is $>|30|$ mV the particles will remain stable in the suspension and not form agglomerates due to their strong similar charges. For lower values of zeta potential, agglomeration may occur, causing the suspension to become unstable.⁹

The pH of the host suspension has a large influence on the zeta potential of a particle. The zeta potential of a particle tends to go more negative when it is placed in basic solutions compared to more acidic solutions, where the charge can be neutralized and eventually become positive. The point at which there is no net charge on a particle is called the iso-electric point (IEP).⁹

The electro-kinetic measurements for ZnS was performed through a recent collaboration with Cornell University¹⁰. The bulk ZnS substrate was characterized using a custom instrument developed by Kirby et al.¹⁰ that measured the velocity of particles as a function of varying electric field magnitude suspended between two thin plates of ZnS that were separated with 50 μ m spacers. The suspending fluid pH was adjusted in order to determine the IEP of the material under test. The IEP of the bulk ZnS surface was measured to be between pH 5-6.

3. POLISHING EXPERIMENTS

For this study, we studied CLEARTRAN™, which is the multispectral grade ZnS with a grain size of 20 – 35 μ m.¹¹ Its mechanical properties are compared to other common visible and infrared materials in Table 1.

Material	Knoop Microhardness	Fracture Toughness	Young's Modulus	Reference
	kg/mm ²	MPa m ^{1/2}	Gpa	
ZnSe	105	0.5	70.0	[2]
CLEARTRAN	160	1.0	74.5	[11]
Fused Silica	460	0.8	72.6	[2]
Sapphire	2200	2.0	344.0	[2]

Table 1 – Mechanical properties of CLEARTRAN and select other infrared materials, in rank order of increasing Knoop Microhardness^{2, 11}

Two ZnS samples used for this work were 40mm in diameter and initially 15mm thick. Typically, experiments such as these are carried out using plano-plano coupons or witness samples in order to make removal rate measurements easier. Nevertheless, with the intention of using any results found during this work to make spherical optics, the surface that was polished had a convex radius of curvature of 75mm. The second side of both ZnS parts was Blanchard ground flat for ease in blocking. The same two samples were used for all of the experiments; they were re-cut to the same radius on an OptiPro eSX-Twin 125.¹²

For each of the experiments, the samples were subjected to the same initial surface treatment. As mentioned above, the eSX-Twin 125 was used to generate a 75mm CX radius, each time removing 200µm of material with a rough diamond tool. The next step was to remove 150µm with a medium diamond tool. The resulting surface quality from the CNC generation step was 6.7 (+/- 1.9)µm PV surface roughness and 0.35 (+/- 0.8µm) RMS surface roughness.¹³ The surfaces were then pre-polished using 3µm alumina aqueous polishing slurry.

Two types of abrasives were used with both median particle sizes ranging from 0.3 – 0.5µm. The polishing laps consisted of synthetic and natural pitch. The first abrasive has an approximate IEP pH value of nine and the second has an approximate IEP pH value of two. A full factorial experiment was run with both of these abrasives at three different pH levels, pH 4, pH 7 and pH 10. The aqueous based slurries were adjusted with a common acid and base. The amount of material removal was recorded as a function of weight loss with an Acculab analytical balance¹⁴ with the precision of +/- 0.1mg. The surface roughness values were measured using a Zygo NewView 7200 white light interferometer with a 20x Mirau objective and four phase averages as shown in Figure 2. Visual surface inspection was also performed as shown in Figure 3.

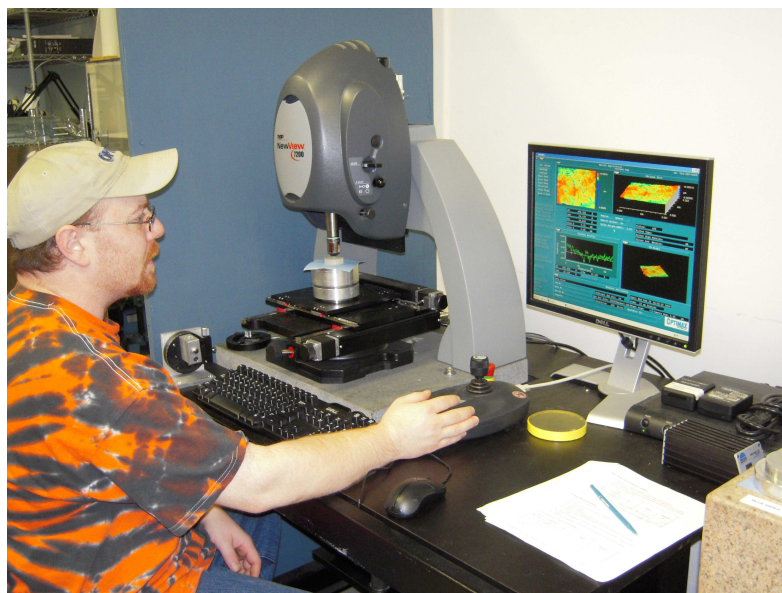


Figure 2 – Surface roughness inspection on Zygo NewView 7200



Figure 3 – Visual surface inspection of ZnS surface

4. PREDICTED RESULTS

Based on the IEP values of the abrasives and ZnS surface, we predict the following surface charge abrasive/surface matrix shown as Table 2. According to Cook's work with oxide abrasives and silicate glasses the highest removal rates will occur at the pH value closest to its IEP which for Abrasive 1 would be pH 9 and pH 2 for Abrasive 2. These two pH values are conditions that will promote abrasive agglomeration. Cumbo's slurry charge control effect predicts that the smoothest surfaces will occur (on silicate glasses) when the slurry pH is higher than the polishing abrasive IEP, which would be at pH 10 for Abrasive 1 and for all of the testing conditions for Abrasive 2. One very big difference between the work here and that of Cook and Cumbo is that they both worked with silicate glasses that have IEP values between 2-3, and ZnS has an IEP of 5.

In general, we predict, that the highest removal rates will occur when the abrasive/surface charges are opposite, and the smoothest surfaces will occur when the abrasive/surface charges are similar. This hypothesis is based on previous results with glass and the model that when the surface and the abrasive particles have opposing charges and hence in a state of attraction, the situation will promote higher removal rates.¹⁵

	pH 4	pH 7	pH 10
Abrasive 1/ZnS	+/+	+/-	-/-
Abrasive 2/ZnS	-/+	-/-	-/-

Table 2 – Predicted abrasive/surface charge matrix

5. EXPERIMENTAL RESULTS

[Note: The experimental results listed in this section do not reflect optimized conditions for conventional polishing of ZnS. The results in this paper indicate the baseline experiments for two abrasives in aqueous solutions at various pH values. These results will be used to begin development of an empirical model and along with subsequently planned experiments, and optimum result is expected to be revealed and published at a later date.]

The removal rate results plotted as a function of slurry pH for synthetic pitch in Figure 4 are extremely unexpected. The highest removal rates occur at pH 4 for Abrasive 1 and pH 7 for Abrasive 2. The slurry pH appears to have very little impact on the material removal rate of ZnS using Abrasive 1, where significant changes in removal rate were observed for Abrasive 2 with slurry pH adjustment.

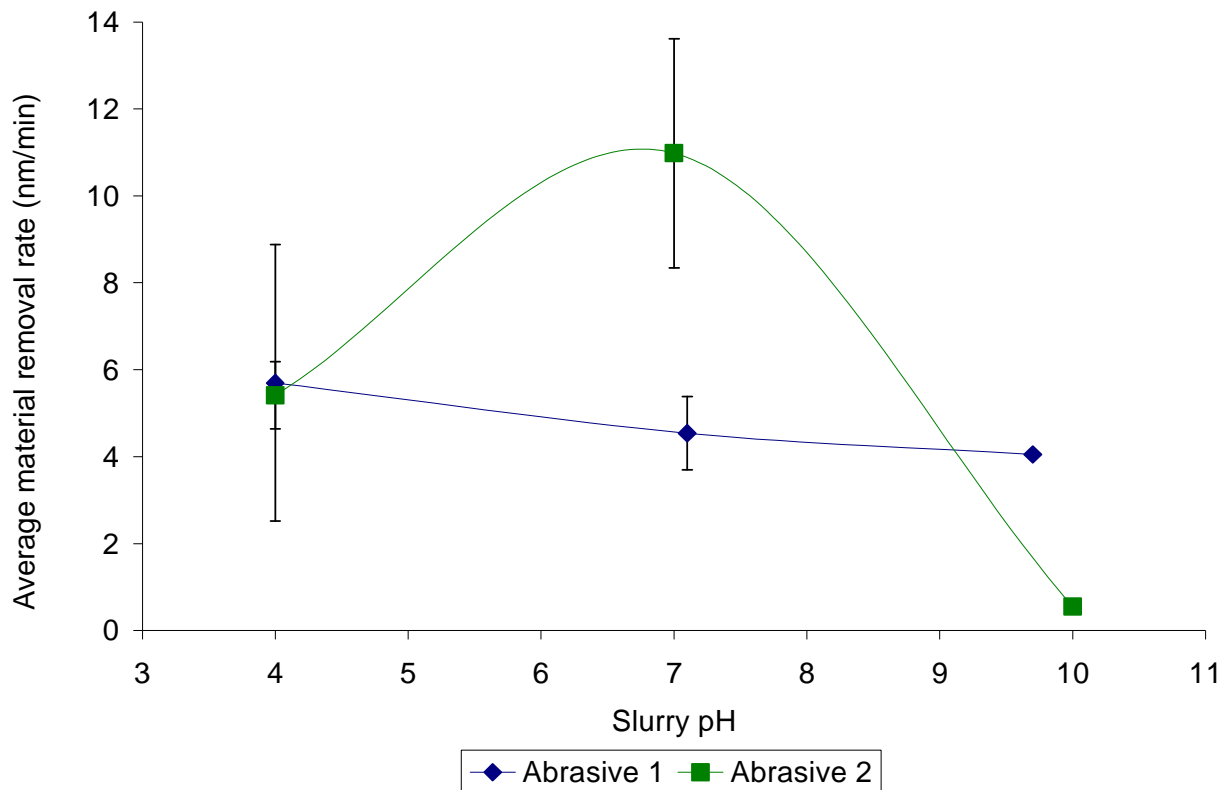


Figure 4 – Average ZnS material removal rate versus slurry pH for Abrasive 1 (IEP 9) and Abrasive 2 (IEP 2). Lines have been drawn between points to guide the eye only.

The results shown in Figure 4 differ from the glass prediction model, may be due to either the ZnS material or the polishing lap material. One hypothesis is that either the polycrystalline nature, chemical composition and/or the higher IEP value of ZnS compared to glass are the main causes of the observed trends as a function of slurry pH. Another is that the lap material is playing a larger role in the removal mechanism, either through its mechanical or possibly chemical interactions.

When this work was originally started, the intention was to keep the pitch type constant. Synthetic pitch was chosen based on its lot-to-lot consistency. Synthetic pitch is a polymer based visco-elastic substance. What we refer to as natural pitch is the “traditional” types of pitch that are either wood or oil based. Figure 5 contains a plot of the data shown in Figure 4 along with removal rate data for ZnS-MS and Abrasive 1 using a natural pitch lap. The natural and synthetic pitch types that were used for this work were equivalent (similar viscosity and hardness) based on the synthetic manufacturer’s product information. (Results are only reported for Abrasive 1, because the Abrasive 2 experiments were not complete at the time of this publication.)

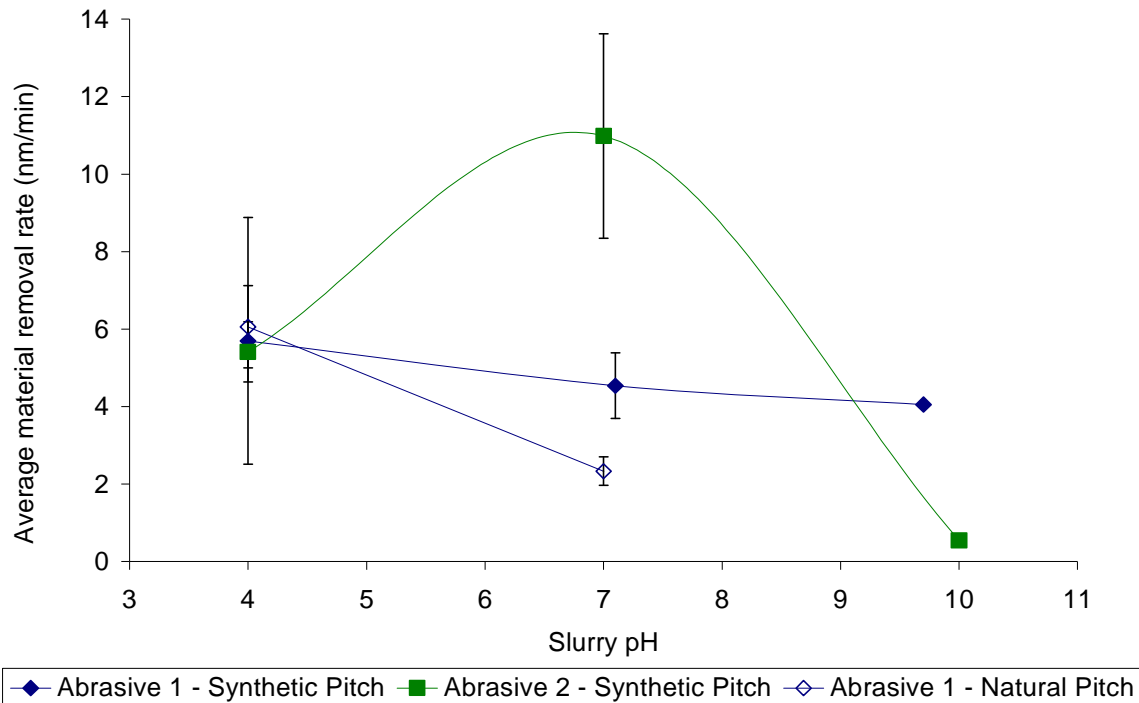


Figure 5 – Average ZnS material removal rate versus slurry pH for Abrasive 1 (IEP 9) and Abrasive 2 (IEP 2) with two different types of pitch. Lines have been drawn between points to guide the eye only.

The trend for the natural pitch versus the synthetic pitch using abrasive one were different. The removal rates were comparable at pH 4, but the removal rate at pH 7 with the natural pitch was significantly lower. The natural pitch experiments are still in progress and the pH 10 data will be presented at a later date. This work was originally completed using synthetic pitch to eliminate batch-to-batch variations, but after similar experimentation with fused silica¹⁶ natural pitch was included in this work as well. Initial results indicate a dependency on pitch type as well as slurry pH for the average material removal rate of ZnS.

The average areal surface roughness measurements plotted as a function of slurry pH for the synthetic pitch are shown in Figure 6. Unlike the removal rate data, the surface roughness trends only differ slightly from the glass model predicted results. For Abrasive 1, the smoothest surfaces occur when the ZnS surface and the polishing abrasive have similar charges, and when they differ the surface roughness values are approximately six times higher. The surface roughness values for Abrasive 2 follow the same trends as that for Abrasive 1, where they peak at pH 7. Due to the fact that the highest removal rates occur at the same pH regardless of abrasive type, it is possible that the zinc sulfide’s dependence on slurry pH is the dominant factor in determining surface roughness value. In order to exclude the synthetic lap material, this experiment was repeated using a natural pitch lap. The data collected to date is shown in Figure 7.

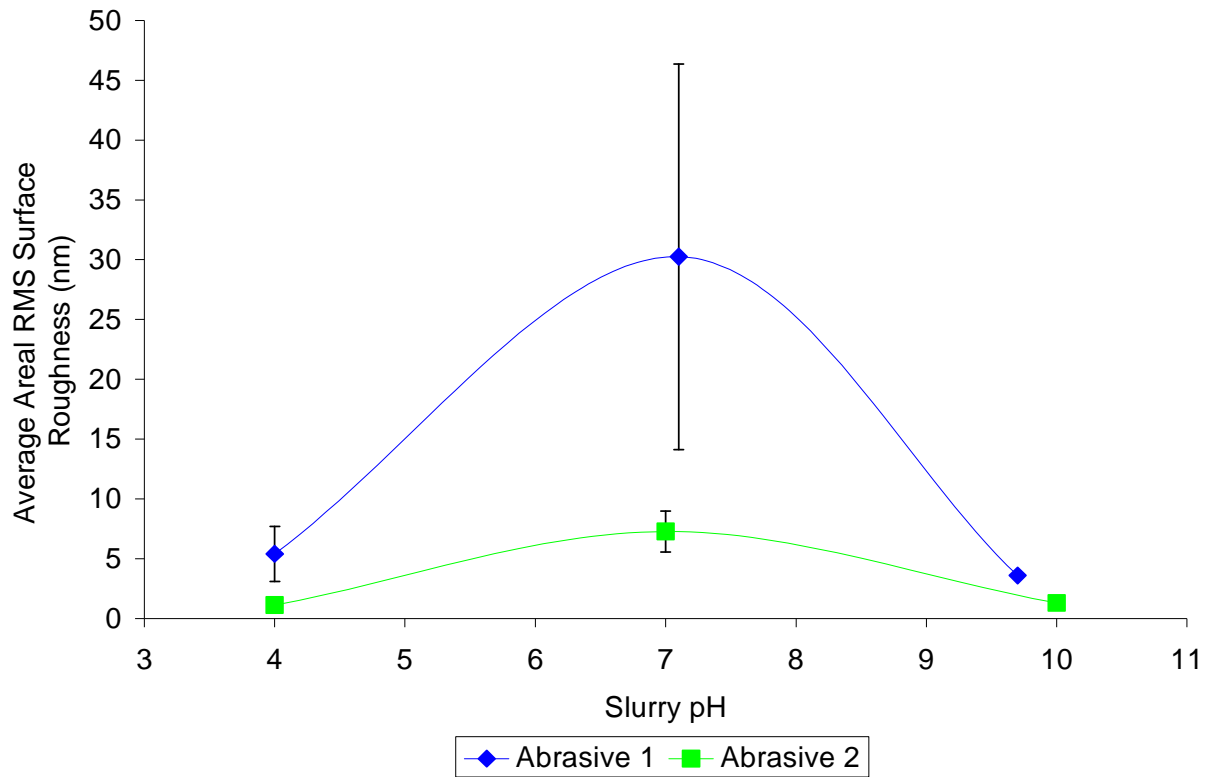


Figure 6 – Average areal surface roughness versus slurry pH for Abrasive 1 (IEP 9) and Abrasive 2 (IEP 2). Lines have been drawn between points to guide the eye only.

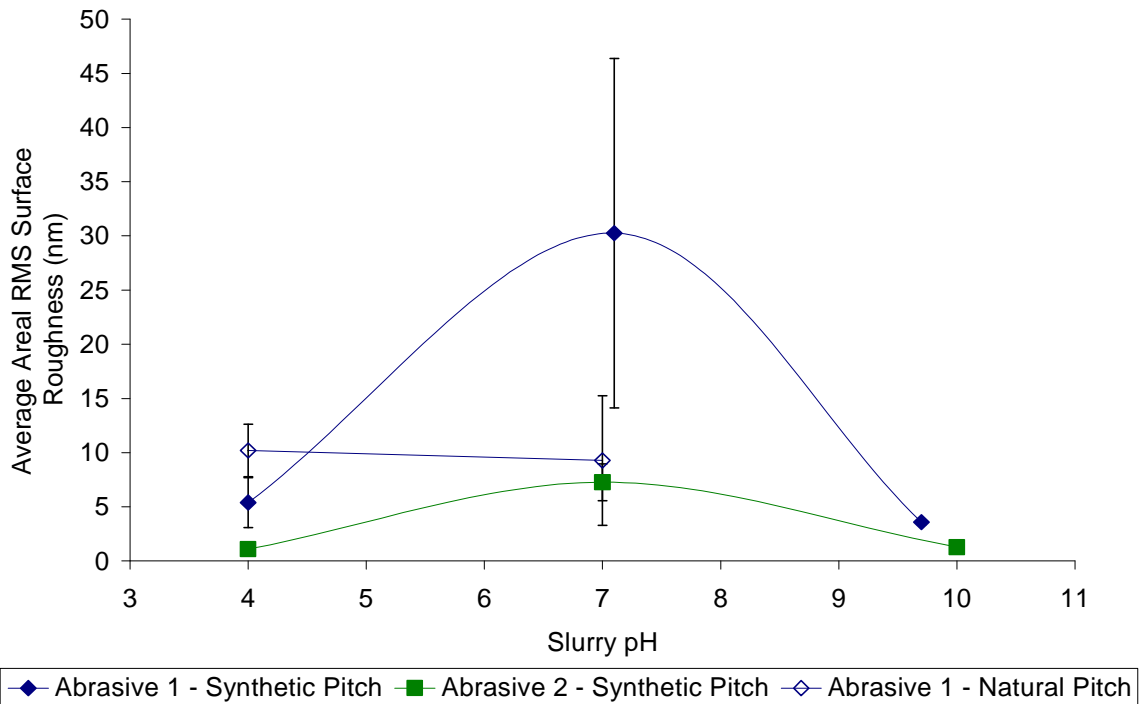


Figure 7 – Average areal surface roughness versus slurry pH for Abrasive 1 (IEP 9) and Abrasive 2 (IEP 2) polished using both synthetic and natural pitch. Lines have been drawn between points to guide the eye only.

With the data collected to date, the surface roughness results from the natural pitch experiment with abrasive one appear to be independent of the slurry pH. This trend is entirely different from the synthetic pitch results.

Figure 8 shows the same surface roughness data, except it is plotted versus the slurry pH minus the IEP of the polishing abrasive. This is shown in order to compare the ZnS-MS results with Cumbo’s slurry charge control effect. As mentioned above, Cumbo predicted that polishing conditions that produce positive values of $pH - IEP_{abrasive}$ would produce smoother surfaces.

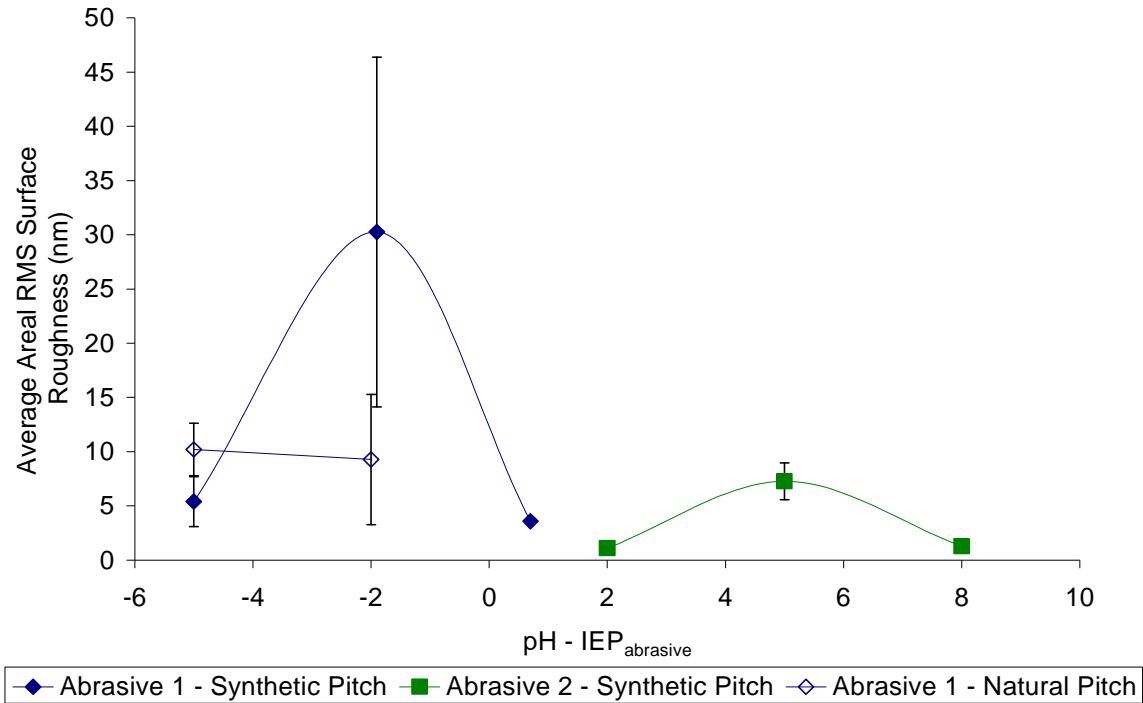


Figure 8 – Surface roughness data versus slurry pH minus the Abrasive IEP. Lines have been drawn between points to guide the eye only.

Upon first glance at Figure 8, one might come to the conclusion that Cumbo’s theory holds for ZnS-MS as well as silicate glasses. However, if we closer examine examples of the Abrasive 2 surface finishes shown as false color surface maps in Figure 9, it is evident from the false color image of the surface polished with pH 7 and Abrasive 2 does not have a desirable surface texture. This again indicates that there are additional interactions at work other than only the slurry pH and the abrasive.

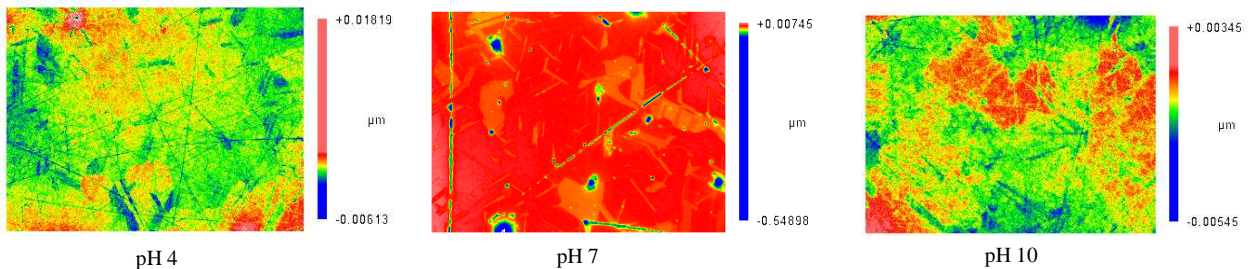


Figure 9 – False color surface maps of the ZnS polished with Abrasive 2 in pH 4, pH 7 and pH 10.

6. CONCLUSION AND FUTURE WORK

This work produced very interesting, yet unexpected results. The results indicate that the electro-kinetic interactions in glass polishing do not correlate for polishing zinc sulfide material using synthetic pitch. There is still a strong dependence for both removal rate and surface roughness on the chemistry of the polishing slurry, even though the ZnS results do not correlate with the glass polishing models. Initial results also indicate that the relationships between the ZnS surface, the abrasive and the pitch lap material are all very important. The next steps in developing a conventional finishing model for ZnS will be to complete the additional testing with natural pitch and then include additional polishing abrasives with varying IEP values and additional polishing lap materials.

7. ACKNOWLEDGEMENTS

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