Exploration of Ion-Exchanged Glass for Seals Applications

Roushan Ghanbari[1], Keith Tolk[2], William Charlton[1]

[1]Nuclear Security Science and Policy Institute
Nuclear Engineering Department, Texas A&M University
College Station, Texas, USA

[2]Milagro Consulting LLC
Akbuqerque, NM, USA

E-mail: rghanbari@tamu.edu, keith.tolk@ktolk.com, wcharlton@ne.tamu.edu

Abstract:

As the nuclear industry grows around the globe, it brings with it a need for more safeguards and proliferation resistant technologies. The International Atomic Energy Agency (IAEA) depends on effective containment and surveillance (C/S) technologies and methods for maintaining continuity of knowledge over nuclear assets. Tags and seals, a subset of C/S technologies, are an area where innovation has been relatively stagnant for the past fifteen years (pickett lecture). Seals are used to maintain the integrity of monitoring enclosures, containers, or perhaps a point of entry. Tags are used like barcodes, as unique identifiers to account for separate items. It is necessary to investigate technologies not previously used in this field in order to defend against emerging threats and methods of defeat.
Based on a gap analysis of tags and seals currently being used by the IAEA, completed with the input of several subject matter experts, the technology selected for investigation was ion-exchanged glass. Ion-exchanged glass is relatively inexpensive, has high strength, and can be used in a variety of applications. If identical pieces of glass are exchanged under the same conditions and subjected to the same point load, the fracture patterns produced can be compared and used as a verification measure. This technology has the potential to be used in passive seal applications.

1. Introduction

As the nuclear industry grows around the globe, it brings with it a need for more safeguards and proliferation resistant technologies. The International Atomic Energy Agency (IAEA) depends on effective containment and surveillance (C/S) technologies and methods for maintaining continuity of knowledge over nuclear assets[1]. Tags and seals, a subset of C/S technologies, are an area where innovation has been relatively stagnant for the past fifteen years[2]. Seals are used to maintain the integrity of monitoring enclosures, containers, or perhaps a point of entry. Tags are used like barcodes, as unique identifiers to account for separate items. It is necessary to investigate technologies not previously used in this field in order to defend against emerging threats and methods of defeat.
Previously, a gap analysis evaluating the tags and seals the IAEA currently uses, along with technologies not developed for used in containment and surveillance applications was developed. This analysis utilized the input of several subject matter experts. The technology selected from this analysis for investigation was ion-exchanged glass. The research presented demonstrates the ability to compare and match fracture patterns of identically ion-exchanged glass disks for verification purposes.

2. Background

The areas of containment and surveillance where the ion-exchanged glass can be applied are important to note and provide a framework for some of the design requirements a device incorporating the ion-exchanged glass may have to meet. Additionally, understanding the process of ion-exchange is necessary in order to take full advantage of all advantages associated with this process.

2.1. Tags and Seals

A seal is a tamper indicating device designed to leave non-erasable, unambiguous evidence of entry or tampering. The purpose of a seal is not to restrict or prevent access but just record that it took place.[1] Seals are mainly used for arms control and material containment, and therefore need field verification and authentication capabilities.
Tags are unique assigned identifiers or intrinsic features that are used for asset identification.[1] The purpose of a tag is to ensure that it is extremely difficult for an adversary to counterfeit an individual identification marker that is applied to, or inherent to an asset.[3] The IAEA uses tags to document individual assets and ensure that unauthorized replacements are not made.

2.2. Ion-Exchanged Glass

The process of chemically tempering glass, or ion-exchanging glass, is accomplished by immersing the glass in a molten solution of potassium nitrate where the Na^+ ions, close to the surface in the glass are replaced buy the K^+ ions from the solution. Figure 1 shows the process of ion-exchange. This process (ion-exchange) is thermally activated and results in the strengthening of the glass.[4,5,6] The increase in glass strength is dependent on the time and temperature at which the ion-exchange occurs.[7]

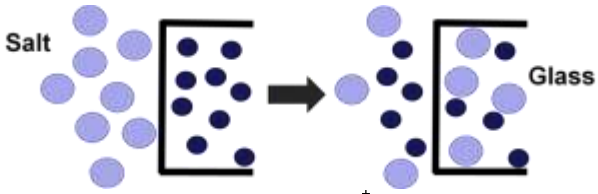

Figure 1. Schematic of the ion-exchange process, the large K^+ ions from the salt solution exchange with the Na^+ ions in the glass

Several papers and presentations concerning the fragmentation of ion-exchanged glass have been published and used as guidelines for the experimental procedures of this study. At present, two papers have been published discussing the fragmentation behavior and crack branching patterns found in ion-exchanged glass; however there has been no work done to match the fragmentation patterns of two identical pieces of glass that were ion-exchanged under the same parameters.[7,8]

2.2.1. Ion-Exchanged Glass Applications

There are several options for using ion-exchanged glass in tag or seal applications for C/S. The simplest application is to use an initially fractured piece of glass as a tag. This would require a piece of glass to be contained, its fragmentation pattern preserved, and the glass attached to an asset and photographed. At a later date the fragmentation pattern would be inspected and compared to the originally documented pattern.
Using ion-exchanged glass in a passive seal would be beneficial for securing the ends of a wire loop between two pieces of glass. The two ends could be sandwiched between two glass disks, of known ion-exchange parameters, and bonded by an adhesive. When the seal is removed from the asset each disk could be fractured and analyzed. This post-mortem inspection would rely on the ability to verify the fracture pattern produced by the disks and compare it to known standards for glass ion-exchanged under the same conditions. Analyzing and verifying the fracture pattern will rely on image analysis which can easily be performed with basic equipment in a lab setting.

3. Fracture Procedure of Ion-Exchanged Glass

The glass used in this study was an alumino-silicate glass, Corning 2317 or Gorilla® Glass. The 2317 glass was ordered as a set of 20 disks, 5.08 cm in diameter and 2 mm in thickness, which underwent ion-exchange in a potassium nitrate bath for 48 hours at a temperature of 450°C (Marathon Glass, Stillwater, MN). The samples were ordered to these specifications in order to minimize possible discrepancies when following the experimental procedures outlined by Tandon and Kooi. [7, 8]

3.1. Experimental Setup and Procedure

The samples were cleaned with acetone and transparent tape was applied to one side of each sample. The samples were marked with a felt tipped pen in the center of the disk on the taped side. This mark was used as a reference for aligning the indenter tip with the center of the samples. The samples were fractured by loading the center of the un-taped surface with a Vickers macrohardness indenter (Buehler Macro Vickers 1900-2005) at 30 kg load, applied at a speed of 70 µm/s and held for 20 s. The tape held the sample fragments together after undergoing the indentation process.

4. Fracture Pattern Analysis

Upon preliminary visual inspection the fractured sample were divided into two groups, those with a '3 leaf' fracture pattern and those with a '4 leaf' fracture pattern. If the samples did not exhibit either of these patterns they were considered a failed sample. One sample was lost during the fracturing process, leaving 19 samples to be evaluated. Table 1 shows the fractured sample number and the respective number of leafs determined by visual inspection. Evaluating this data, based on a total of 19 samples 68.42% of samples fractured in a '4 leaf' pattern, 26.32% fractured in a '3 leaf' pattern, and 5.26% of the samples failed. Effectively, this grouping produced two samples groups, '3 leaf' and '4 leaf' fracture patterns.

Sample Number	Number of Leafs
1	4
2	Lost
3	4
4	4
5	4
6	3
7	4
8	Failed
9	4
10	4
11	4
12	3
13	3
14	3
15	4
16	4
17	4
18	3
19	4
20	4

Table 1. Fractured Sample Number and Corresponding Number of Leafs

4.1. Image Analysis

Image analysis of the fracture patterns utilized the Image Processing Toolbox in MATLAB. A code for image alignment and spatial transformation took advantage of the Control Point Selection Tool, allowing the user to interactively select points on a pair of images (MATLAB help). In each comparison one image is defined as a 'base' image while the other is the 'unregistered' image. The 'unregistered' image will undergo the spatial transformation for the control point pairs in each image to be aligned and is ultimately displayed with a semitransparent overlay of the 'base' image for comparison as seen in Figure 2. This image provides a visual reference but is not substantial for fracture pattern authentication or verification. It should be noted that fracture pattern comparisons were only performed with samples of the same group.

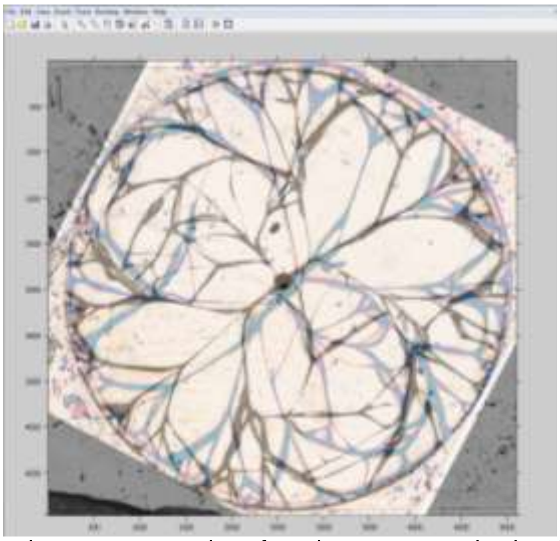

Figure 2. Semitransparent overlay of two images created using the MATLAB

The images are also analyzed in ImageJ, an image analysis software developed by the Research Services Branch of the National Institute of Health. The images can be imported from MATLAB, already overlaid, or can be manually rotated, translated, and overlaid. A desired pair of images can be combined using the XOR function, this function uses pixel addition displaying two overlaid black pixels as white. This means where two cracks are aligned white pixels will be seen. The mathematical expression of this composite image, assuming image A and image B is:

$$(A-B)\cup(B-A) \qquad \text{Eq.1}$$

An example of a composite image is shown in Figure 3. Thus, evaluating the number of black pixels compared to white, gives a percentage for determining how similar the fragmentation patterns are between two images.

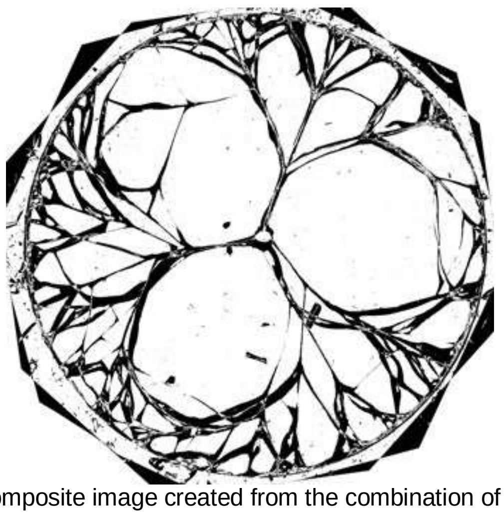

Figure 3. Composite image created from the combination of two images.

This percentage of black to white pixels evaluation is achieved by defining a circular area of 0.200 inches (0.5 inch diameter) about the center of the resultant image. The analysis was performed on the central region of the images to avoid edge effects, where the sample underwent ion-exchange on three surfaces which produces a greater degree of fragmentation.[8]

5. Results

Basic statistical analysis, using the software Minitab, was done on the fractured samples. Probability plots, histograms, and other data characterizations were produced for both the '3 leaf' and '4 leaf' datasets. These characterizations provide a sound basis for deducing meaning from both datasets. The '3 leaf' dataset had a total of 5 samples, providing 10 combinations of images; the data shown in Table 2 is a summary of specific characteristics. Among these specific characteristics are skewness which measures the lack of symmetry in data, and kurtosis which determines whether data is peaked or flat, relative to a normal distribution. These characteristics can be displayed using a histogram with a normal fit overlay, as seen in Figure 4. The same analysis was done on the '4 leaf' dataset of 13 samples, and 78 image combinations; the data is displayed in Table 3 and Figure 5.

Mean	16.181%
Standard Deviation	2.661%
Variance	0.00071
Skewness	-0.311
Kurtosis	-0.259

Table 2. Characteristics of '3 leaf' Composite Images

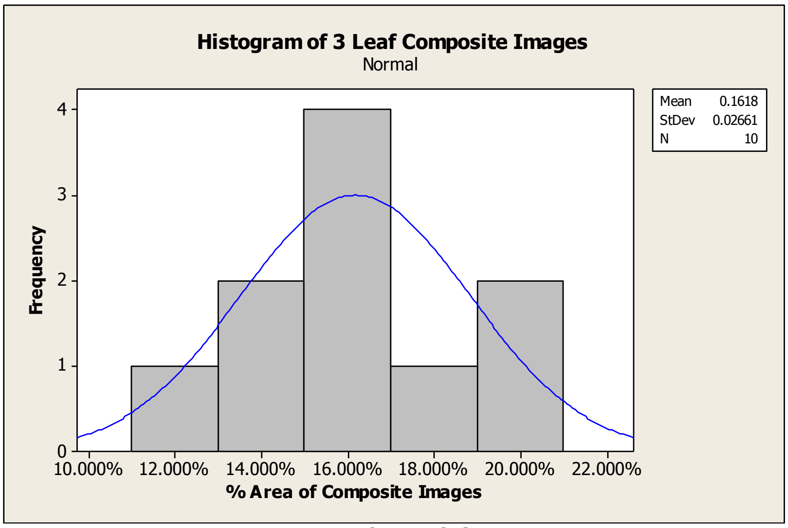

Figure 4. Histogram of '3 leaf' Composite Images

Mean	20.543%
Standard Deviation	3.448%
Variance	0.00119
Skewness	-0.251
Kurtosis	-0.695

Table 3. Characteristics of '4 leaf' Composite Images

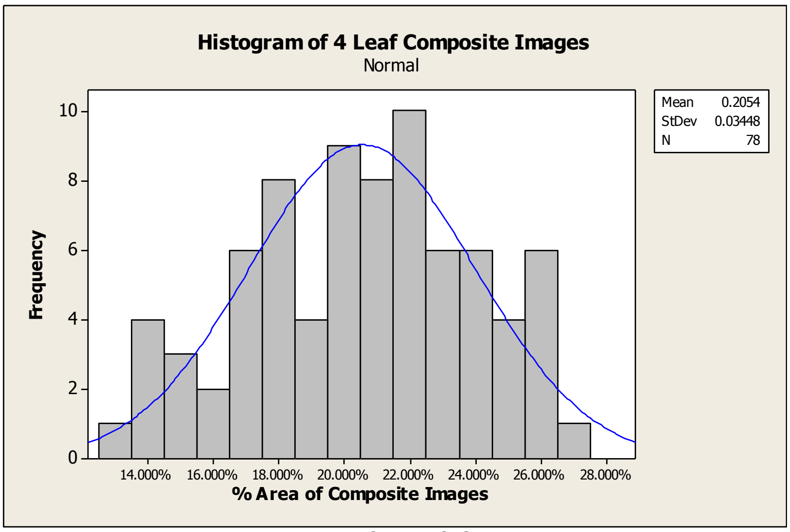

Figure 5. Histogram of '4 leaf' Composite Images

The histogram of the '3 leaf' composite images will not provide much useful data, given that the dataset is only 5 samples. The histogram of the '4 leaf' composite images displays a larger spread of data and it complements the overlaid normal fit. It is interesting to note that both data sets are skewed to the left and are considered flat relative to the standard normal distribution.

It is important to simulate the post-mortem verification technique for glass seals if they are deployed in the field. One method to simulate this analysis is to select a sample from the '3 leaf' or '4 leaf' populations; this will be called the 'field' sample. The samples not selected from the respective populations will be the 'control' samples.

The composite images created with the field sample and the control samples from the respective population were analyzed. The percentage of black to white pixels , or the% Area, for each composite image was computed and the average calculated. Composite images of the control samples from the populations were produced for all possible remaining combinations and the % Areas calculated and averaged. This process is repeated for each sample in the respective populations.

The difference between the averaged % Areas of the field and control samples was calculated and compared to the standard deviation (± σ) of the correlating population. If the difference is less than or equal to the standard deviation the field sample is considered a match to the controls, this is shown in Figures 6 and 7. The majority of the data points fall within one standard deviation, giving an 60% pass rate for the '3 leaf' fracture patterns and a 78% pass rate for the '4 leaf fracture patterns.

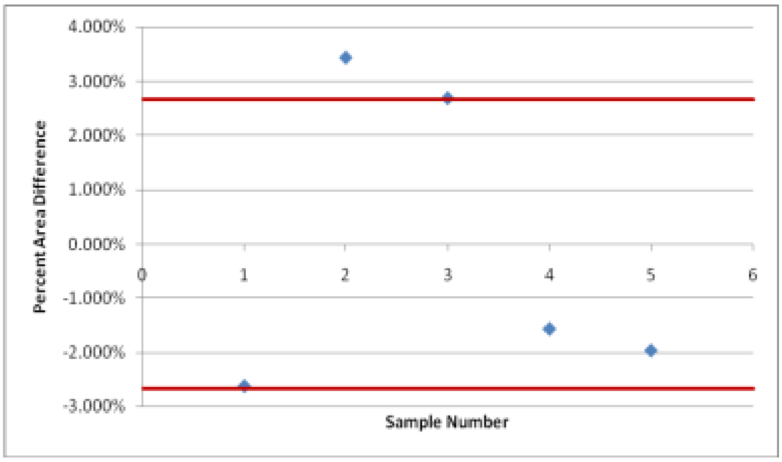

Figure 6. Comparison of '3 leaf' % Area Differences to One Standard Deviation

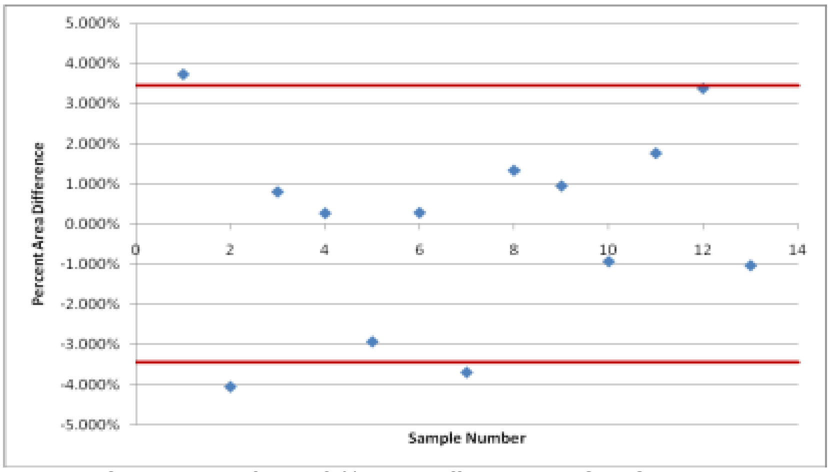

Figure 7. Comparison of '4 leaf' % Area Differences to One Standard Deviation

6. Conclusions

Based on the preliminary results it appears that ion-exchanged glass is a viable technology for a tag or seals application. Although more statistical tests need to be done pass rates of 60% and 78% for one standard deviation at a 95% confidence interval should not be discounted. A larger sample population needs to be assessed in order to validate these findings. Indeed further study necessitates another sample group that has undergone the ion-exchange process with different parameters to truly evaluate the possibility of verifying glass based on distinct fracture characteristics.

7. Acknowledgements

The authors would like to acknowledge Dr. Eric Taleff at The University of Texas at Austin for the use of his laboratory facilities, Dr. Stanislav Vitha at the Microscopy and Imaging Center at Texas A&M University for his time and expertise. In addition a special thanks and acknowledgment goes to Dr. Raj Tandon at Sandia National Laboratories for his expertise.

9. References

1. *Safeguards Techniques and Equipment*, 2003 Edition, International Atomic Energy Agency (2003).
2. Pickett C, Richardson G, *Seal Selection and Performance: "What Makes a Good Seal, Good"*, ORNL.
3. Tolk K, *Random Patterns and Biometrics for Counterfeit Deterrence*, Sandia National Laboratories, SAND 93-24704, 1993.
4. Gy R, *Ion Exchange for Glass Strengthening*, *Materials Science and Engineering: B*, **149**, p 159-165, 2008.
5. Kistler S, *Stresses in glass produced by nonuniform exchange of monovalent ions, Journal of American Ceramic Society*, **47**(2), p 59, 1962.
6. Nordberg M.E., Mochel E.L., Garfinkel H.M., and Olcott J.S., *Strengthening by ion exchange, Journal of American Ceramic Society,* **47**(5), p 215, 1964.
7. Tandon R and Glass S.J., *Controlling the Fragmentation Behavior of Stressed Glass, Fracture Mechanics of Ceramics,* **14**, p 77-91, 2005.
8. Kooi J.E. et al, *Analysis of Macroscopic Crack Branching Patterns in Chemically Strengthened Glass, Journal of Materials Research,* **23**, p214-225, 2008.