EFFICIENCY AND QUALITY IN A BATCH TREATMENT: THE CONSERVATION OF OVER A HUNDRED LEATHER SHOES AND FRAGMENTS.

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Abstract

In late 2008 nearly 400 organic objects from the Old Songhees Reserve site in Victoria, British Columbia, arrived at the Canadian Conservation Institute for treatment. Over half of these objects were leather shoes and fragments covered with corrosion and heavily iron stained. The treatment of 112 of these objects is the topic of this paper. Treatment included individual mechanical cleaning of each shoe, followed by mass chloride removal, iron corrosion stain removal, impregnation with polyethelyne glycol, reshaping, freeze drying, and final consolidation and repair. Employing batch treatment methods for many of the conservation steps reduced time and material costs while careful planning, balanced decision making and monitoring meant that the quality of treatment was not reduced.

Keywords: leather, iron staining, iron corrosion, batch treatment, chlorides, efficiency, ammonium citrate

1. THE OLD SONGHEES RESERVE & OBJECTS

1.1 *Old Songhees Reserve*

Located in the Inner Harbour of Victoria, British Columbia, the Old Songhees reserve was a prominent and important part of the city from 1843 to 1911. Historically much of the city of Victoria was Songhees territory. When Fort Victoria was built in the 1840s the Songhees families created one village in the Inner Harbour. This village was sometimes referred to by Europeans as Lekwungen, or Stamish Village. In late 1844, the village moved to the other side of the harbour and became a reserve (Keddie 2003). The reserve, the home of the Songhees people, grew over time to become a center for other visiting native peoples from the coastal and northern areas of British Columbia. Until the reserve was relocated in 1911, the Old Songhees Reserve was a meeting place, a location for celebrations and a center for trade in Victoria.

1.2 *The Objects*

The objects at the Canadian Conservation Institute (CCI) from the Old Songhees Reserve site (Borden Number DcRu-25) were recovered during archaeological investigations preceding the construction of a spa and residences. The leather objects described in this paper were found in a metal cistern located in a small ravine on the site. It was suggested by the archaeologists that the items in the metal cistern may have been "*dumped shortly after the smallpox epidemic of 1862 in an effort to sanitize the sit*" (I.R Wilson Consultants Ltd. 2006). An assessment of the possible personal hazards associated with treating objects connected to an infectious disease was carried out and it was determined that the probability of viable smallpox bacteria was very low.

The cistern itself had disintegrated onto the objects resulting in heavy iron corrosion products and staining on the leather surface, and interiors. Some pieces of leather were embedded in remaining fragments of the cistern. Apart from the damage due to the presence of corrosion products, other physical and chemical deterioration was apparent;

- visible and heavy chloride contamination
- waterlogged condition
- exposure of the leather grain
- splitting and cracking
- crumbling and fragmentation of exposed edges
- severe warping and folding
- areas of loss

Figure 1. Visible chlorides on the surface of a sole

Figure 2. Section of a shoe showing many signs of severe deterioration

2. CREATING A BATCH TREATMENT

These objects arrived at the laboratory in late 2008. The leather objects numbered over 200, and the first treatment was carried out on 112 of the shoes and larger shoe fragments. To develop and implement an efficient batch treatment, the steps, methods, and materials needed to be well planned and researched prior to beginning the work to ensure that all possibilities were anticipated and the project flowed at a good pace. This batch treatment plan needed to address the needs of all objects and ensure the use of reliable and compatible materials. The final plan included mechanical cleaning of the solid corrosion, iron corrosion stain removal, chloride removal, impregnation, reshaping, drying, consolidation and minor repairs . After searching the literature and consulting with other staff, the following treatment steps and materials were chosen based on positive recommendations, previous success rates and ease of use.

1. Sorting of objects into two groups to allow for the continuous treatment of objects.
2. Full immersion in water to begin the process of chloride removal, and to ensure the objects were completely waterlogged.
3. Removal of corrosion products and other debris from the surface and interior of objects using a Cavitron ultrasonic dental scaler, dental tools, and brushes in running water.
4. Immersion of cleaned objects in monitored chloride removal baths.

5. Immersion of cleaned objects in a 2% w/v solution of dibasic ammonium citrate (diammonium citrate or citric acid diammonium salt) in water to remove iron corrosion stains.
6. Impregnation of de-chlorinated objects with a 20% v/v solution of polyethylene glycol (PEG) 400 plus 1% v/v of Hostacor IT to inhibit the corrosion of iron nails and other fasteners of iron and copper.
7. Reshaping of objects using Ethafoam inserts and stretchy medical bandages.
8. Drying of objects using a vacuum freeze dryer.
9. Further reshaping following drying using a Preservation Pen and Bionaire ultrasonic humidifier.
10. Consolidation of friable areas using a 2% w/v solution of Klucel G in ethanol applied by brush or syringe.
11. Repairs and reinforcements using reactivated strips of Reemay coated with a 50:50 w/w mixture of Lascaux 498 HV and 360 HV.

The properties of some of the materials and why they were chosen will be discussed in greater detail in the remainder of this paper.

3. TREATMENT

3.1 *Mechanical Cleaning*

The corrosion products on the surface of these objects were well bonded to the leather. This prevented the safe mechanical removal of this material using small hand tools. The Cavitron ultrasonic dental scaler, which is regularly used when cleaning waterlogged organics, was employed with varying tips and power settings to efficiently remove corrosion products. As is visible in Figure 3, this tool was very effective in liberating the shoes from the heavy iron corrosion. While time consuming, Mardikian et al (2004) pointed out that leather with corrosion products on the surface must be thoroughly mechanically cleaned in order to achieve good results from chemical removal of iron corrosion stains.

Figure 3. Child's shoe before and after mechanical cleaning

3.2 *Removal of Chlorides*

The objects from this site were heavily impregnated with chlorides, some of which had precipitated on the surface prior to arrival at CCI. Based on the visible level of contamination it was necessary to create a treatment step dedicated to monitored chloride removal. Chlorides can act as a catalyst for the production of sulphuric acid causing solubilisation of collagen (M-L.E Florian 1987). It can also cause physical damage to the structure as it precipitates on the surface.

The removal of chlorides was carried out through the immersion of the artifacts in successive 75 L tap water baths. A submersible pump was placed in the bath and a timer was used to agitate the water for one hour , four times a day. This agitation reduced the concentration of chlorides surrounding each object and increased the rate of desalination, while the intermittent running of the pump avoided heating the water, and subjecting the leather to high temperatures, which might cause shrinkage and mold growth. The conductivity of the bath was monitored regularly using a Hanna Dist WP Conductivity/TDS instant read meter. Once equilibrium was reached the water was changed. This was carried out until there was no increase in conductivity after a bath change - a total of 3 months for Group 1, and 2 months for Group 2. While Group 1 was being de-chlorinated Group 2 was cleaned. The bulk of the chlorides were removed from the objects at this point, and it was likely any remaining chlorides would be removed during chemical corrosion stain removal and impregnation with PEG (McLeod et al, 1987).

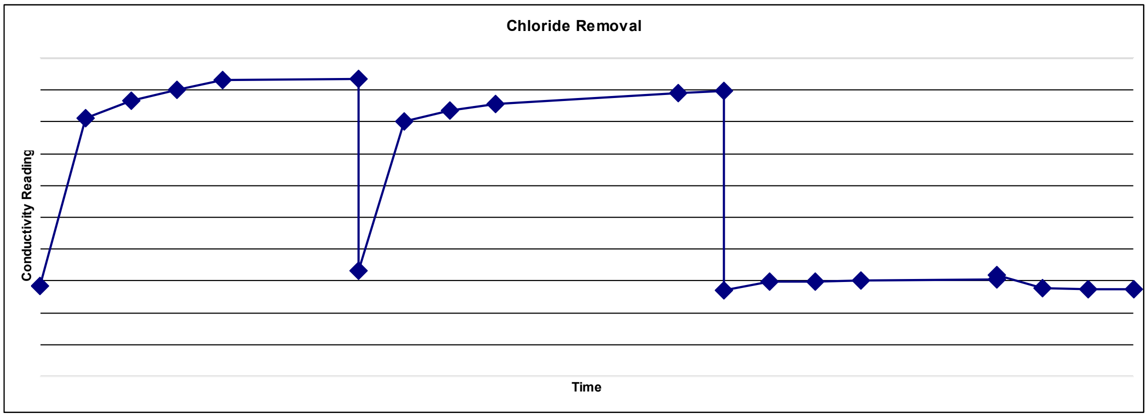


Figure 4. Conductivity graph indicating changes in the chloride content of the leather objects.

3.3 *Removal of Iron Corrosion Stains*

When considering the removal of iron corrosion stains from these shoes several options presented themselves.

1. Do nothing. Leave the stains in place as they may be beneficial to the leather (Bardet et al 2009) and the need for removal is mainly aesthetic.
2. Remove the stains as, it was best stated by Wight (1978), iron stains may often become centers for accelerated chemical and physical decay of the substrate.
    a. Remove the stains using a 2% w/v solution dibasic ammonium citrate (Newton 1987, MacLeod et al 1993, Godfrey 2001, Mardikian et al 2004) followed by thorough rinsing.
    b. Remove the stains using a 5% w/v sodium dithionite solution (SDT) (sodium hydrosulphite or sodium sulfoxykate) combined with a 2% w/v ehylenediaminetetraacetic acid solution (EDTA) (Selwyn & Tse 2008) followed by thorough rinsing.

Option 1, to leave the stains in place, was not chosen. It was decided that the stains should be removed to prevent any future problems.

Sodium dithionite removes iron corrosion stains very effectively but decomposes very quickly, as the acidity of the solution increases due to reaction with water and oxygen (Selwyn, Tse 2008). Based on the high level of corrosion staining on the leather and the limited working time of the solution each shoe would have to be individually immersed in a sodium dithionite/EDTA solution several times to achieve the desired results. To carry out this process several times for 112 objects would require an immense amount of materials, resources, and time.

Ammonium citrate, though not as strong a sequestering agent, is an effective chelate. Both dibasic (pH 4.5 - 5.5) and tribasic (pH 7.0) ammonium citrate solutions were tested for effectiveness, and the dibasic was found to remove more iron stains from these particular objects. It is known that the higher the pH the stronger the chelate, but pre treatment testing seemed to show otherwise with these objects. When discussing the use of low pH ammonium citrate solutions on leather Rabin (1983) states that " *the increased potential of the solution may be due more to the acidity than the material's ability as a chelate*". A pH of 3-6 is considered safe when working with leather (Ganaris, H., 1982), so it was decided to use the more effective dibasic ammonium citrate. The objects would be monitored for signs of deterioration.

A 2% w/v solution of dibasic ammonium citrate was prepared in a large polyethylene tub. As in the case of the chloride removal a submersible pump was inserted with the objects to circulate the solutions at timed intervals. One stained and heavily degraded shoe was chosen for monitoring from each group. Over-softening and crumbling of the leather would indicate deterioration was occurring in the solution~~.~~

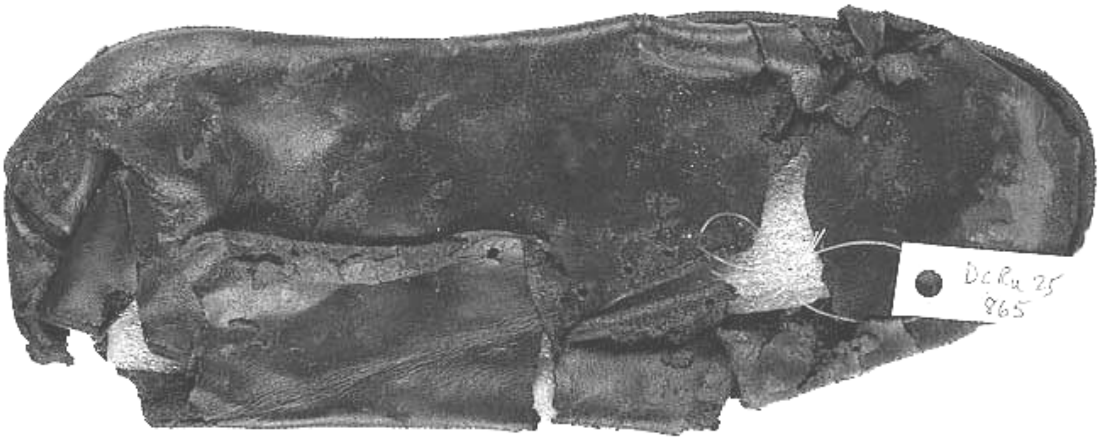
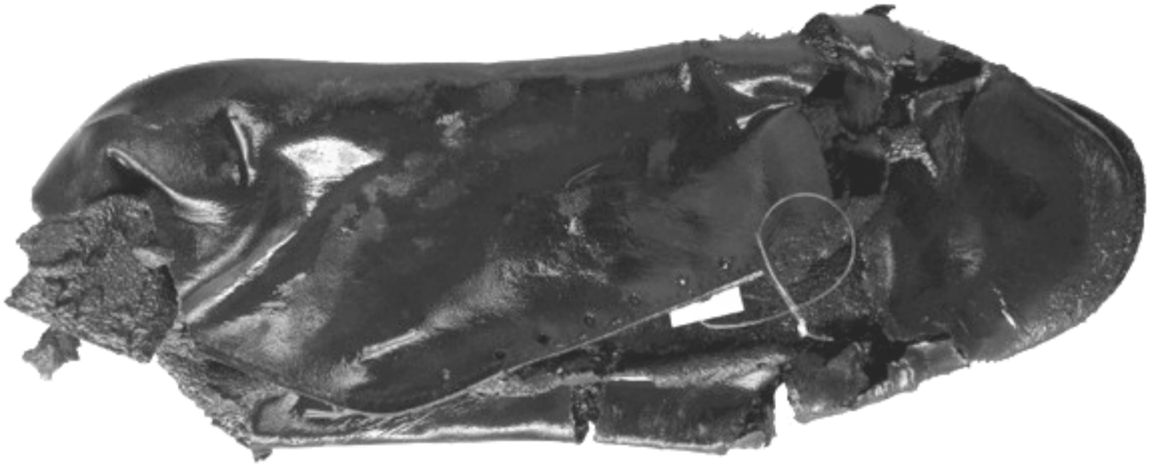


Figure 5. Shoe before and after mechanical cleaning and iron stain removal.



The reduction in staining of the object and colour of the solution were monitored daily for change. Once the changes had ceased, the objects were thoroughly rinsed in running tap water for several days. The rinse water was also monitored for colour change and the rinsing was complete when the water was clear. A new solution of ammonium citrate was prepared and the objects were re-immersed. After two immersions in ammonium citrate the stains were significantly reduced and no further stain removal was required. Following further rinsing, it was assumed that any chelate remaining in the leather ~~it~~ would be removed during immersion in the polyethylene glycol solution.

This method was very effective in removing the iron corrosion staining from the leather objects with no detrimental effects.

	Time displayed in days			
Group	**Immersion 1**	**Rinsing**	**Immersion 2**	**Rinsing**
1	**5**	**9**	**4**	**10**
2	**5**	**5**	**4**	**10**

Table 1. Length of immersion and rinsing cycles during iron corrosion stain removal

3.4 ***Polyethylene Glycol Impregnation and Vacuum Freeze-drying***

3.4.1 *Polyethylene glycol*

A 75L 20% v/v solution of PEG 400 was prepared and Hostacor IT (1% v/v) was added to prevent the PEG induced corrosion of any metal attachments. The solution was monitored for darkening and biological activity. Two of the largest objects from each group were chosen for weight monitoring to determine when PEG uptake was complete. For both groups this step took a little over two and half weeks.

The solution did darken significantly, which may have been caused by the leaching of tannins by residual ammonium citrate, or the acidic PEG solution (Mardikian 2004). Consultation with colleagues, however, suggested that the solution was only slightly darker than normal when treating large amounts of leather (Personal communication). When removed from the bath the objects were briefly rinsed to remove excess PEG from the surface.

3.4.2 *Reshaping*

Before freeze-drying, all the shoes and soles were reshaped and supported while still wet using stretchy medical bandages (Supercrinx), various thicknesses of Ethafoam, and cotton twill tape. The shoes were then frozen.

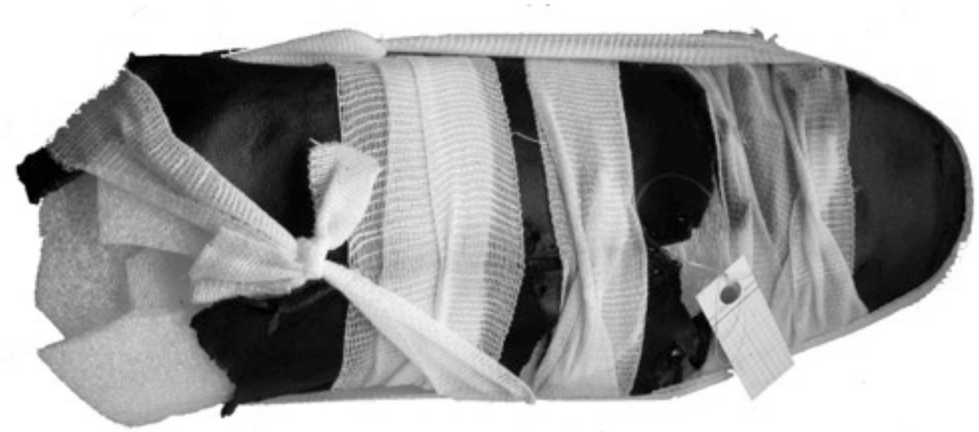


Figure 6. Shoe displayed in Figure 5 after having been reshaped using Supercrinx and foam

3.4.3 *Freeze Drying*

The capacity of the freeze drier at the Canadian Conservation Institute allowed all of the objects in each group to be dried together. The specimen chamber was -25 C, the condenser was -73 C and the pressure was 1.5 Pa. The leather objects required from three days to two weeks to freeze-dry. During this time the objects were monitored and as the weights stabilized objects were removed.

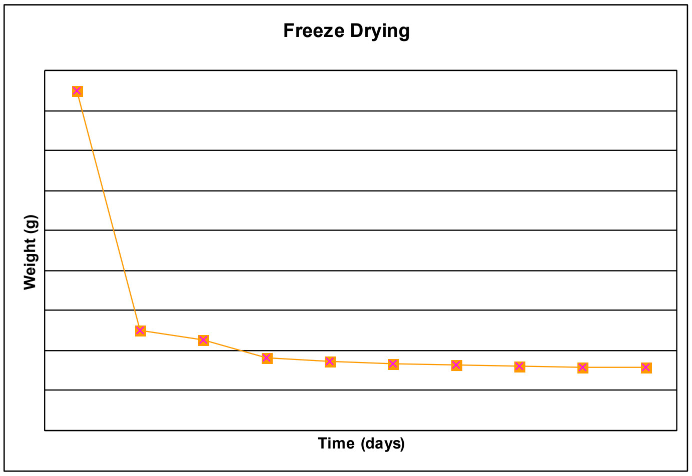


Figure 7. Graph displaying moisture loss from leather during freeze drying.

The slight moisture gain after removal from the freeze dryer was also monitored and objects were left in the lab environment until the weight stabilized. The shrinkage of flat objects, such as soles and other small fragments were assessed through the measurement of the surface area before and after freeze-drying, expressed as a percentage. For example, the sole to the above shrank 7.7% based on the change in surface area. Calculations show the average shrinkage of these objects to be between 7 and 10%.

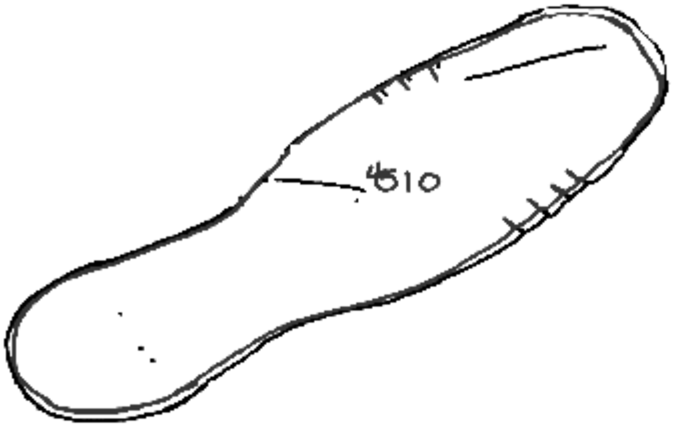


Figure 8. Tracing of a sole before and after treatment to record shrinkage.

3.5 *Further Stabilization*

Following freeze drying many of the shoes required further reshaping, consolidation, adhesion, and support.

3.5.1 *Reshaping*

Using a Preservation pen humidifier, light humidity was applied to misshapen areas of the objects and the objects were reshaped. Foam and weights were used to hold the leather objects in their new shape until dry.

3.5.2 *Consolidation*

On the dry and friable leather grain, and areas where delamination or loss of the original surface had occurred, a 2% w/v solution of Klucel G in ethanol was applied as a consolidant. Based on the frequency of its use in leather conservation, the viscosity of the solution, the extent of penetration and the ease of preparation and application Klucel G was the best material for the task. The fluid solution was applied by brush or syringe.

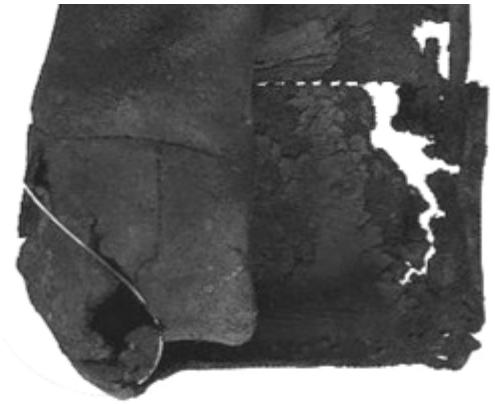


Figure 9. Heel area of a boot upper after consolidation

3.5.3 *Adhesion and Support*

Tears, joins, and weak areas requiring support were reinforced using Lascaux 360HV and 498HV on Reemay paper. A 50:50 w/w mixture of the two Lascaux products was applied by brush to the Reemay on a sheet of Mylar. This was then set aside to dry. When needed, strips of any size were cut from the sheet and reactivated using acetone. Once reactivated, small strips were put in place using tweezers and dental tools, while large strips or "patches" were applied by hand using a silicone release paper backing. Release paper was set on top of the strip or patch and weights were placed to ensure good contact between the adhesive and the leather. When partially dry the weights and release paper was removed.

Once dry, these repairs were coloured using the same 50:50 mixture of Lascaux products tinted with acrylic paints. The repairs were tinted a compatible colour so they would not catch the eye, but would remain easily distinguishable.

Figure 10. Shoe displayed in Figures 5 & 6 after treatment

4. EFFICIENCY AND QUALITY OF THE TREATMENT

By employing well planned treatment steps and thoroughly researched materials the batch treatment of these objects required far less time than previously estimated. Using the official estimate for this project nearly ten weeks were saved. Reducing the time for treatment did not reduce the overall quality of the work. This was determined using a numerical evaluation of the objects by the author and peers.

Traditionally the amount of shrinkage is one factor used to determine the success of a leather treatment along with an assessment of the colour, surface texture and flexibility. This assessment visually evaluated other parameters such as change in shape, friability, delamination, staining, and corrosion products present. A system employing values between 6 and 1 was chosen, and the following defined the worth of each number.

6. Excellent condition: no negative shape change, surface not friable, no delamination, no staining, no corrosion products.
5. Good condition: minimal or no negative shape change, surface not friable, no delamination, no or very minimal staining, no corrosion products.
4. Standard: some negative shape change, minimal areas of friable surface, little or no delamination, minimal staining, no corrosion products.
3: Tolerable: some negative shape change, minimal to moderate areas of friable surface, little to moderate delamination, minimal to moderate staining, some corrosion products may be present.
2: Deteriorated: moderate negative shape change, moderate areas of friability, moderate delamination, moderate staining, corrosion products may be present.
1: Severely deteriorated: severe negative shape change, moderate to severe areas of friable surface, moderate to severe delamination, moderate to severe staining, corrosion products may be present.

Each object was evaluated and assigned a *before treatment* and *after treatment* value, and these values were then compared individually and overall. Colleagues were asked to evaluate a selection of 10 shoes. Qualitatively this assessment proved that the batch treatment was successful, with 95% of the objects moving from the lower to the higher half of the value scale, by at least two value markers. In all cases the condition of each object was significantly improved.

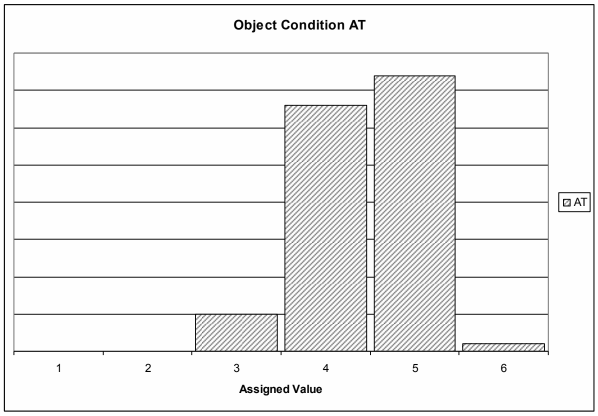
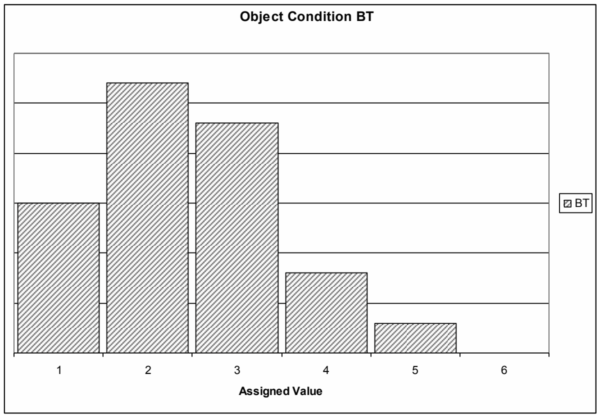


Figure 10. Graphs displaying the recorded shift in condition of these objects.



5. CONCLUSION

The balance that was found between object needs and batch steps lead to the success of this treatment. The methods and materials employed effectively allowed for the desalination, cleaning, stain removal, impregnation and stabilization of over one hundred leather objects and created a well developed treatment for leather objects from this site. Batch treatments are not new, but achieving good results with reduced resources (supplies, space and staff) is becoming increasingly necessary in today's work environment.

Employing batch treatments allows for greater output while not comprising the quality of the work. With proper planning batch treatments can be used to address the treatment of a range of objects of the same material type but varying in condition.

REFERENCES

Bardet, M. et al, (2009), Nuclear Magnetic Resonance and Electron Paragmagnetic as Analytical Tools to Investigate Structural Features of Archaeological Leathers, Analytical Chemistry, Volume 81, No. 4, 2009, pp 1505-1511.

Fawcett, E., (1912), Some reminiscences of old Victoria (1912), Toronto, W. Briggs.

Florian, M-L.E., (1987), The underwater environment; Deterioration of organic materials other than wood, in Pearson, C. (editor), Conservation of Marine Archaeological Objects, London, Butterworths, 1987, pp 44-46.

Godfrey, I. et al, (2002), Iron Removal from Waterlogged Leather and Rope Recovered from Shipwreck Sites, in Hoffman, P. et al (editors), Proceedings of the 8th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven, International Council of Museums, Committee for Conservation Working Group on Wet Organic Archaeological Materials, 2002, pp. 439-470.

Keddie, G., (2003), Songhees Pictorial: A History of the Songhees People as Seen by Outsiders, 1790-1912, Victoria, Royal British Columbia Museum.

MacLeod, I. D., Fraser, F.M., and V.L. Richards, (1989), The PEG-water solvent system: effects of composition on extraction of chloride and iron from wood and concretion, in MacLeod, I.D. (editor), Conservation of Wet Wood and Metal, Freemantle, Western Australian Museum, 1989, pp 245-263.

MacLeod, I. et al, (1994), Observations on the extraction of iron and chloride from composite materials, in Hoffman, P. et al (editors), Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven, International Council of Museums, Committee for Conservation Working Group on Wet Organic Archaeological Materials, 1994, pp. 199-211,

Mardikian, P., et al, (2005), A Preliminary Investigation into the Effects of Diammonium Citrate on Waterlogged Leather from the H.L Hunley Submarine (1864), in Hoffman, P. et al (editors), Proceedings of the 9th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven, International Council of Museums, Committee for Conservation Working Group on Wet Organic Archaeological Materials, 2005, pp 513-531.

Newton, C.L., (1987), Chemical Cleaning of Wet Leather, Journal of the International Institute for Conservation – Canadian Group, Ottawa, Vol 12, 1987, pp 3-8.

Rabin, P.M., (1983), A Study of Iron Stain Removal from Marble Using Various Chelating Agents, Kingston, Queen's University.

Selwyn, L. and S. Tse, (2009), The chemistry of sodium dithionite and its use in conservation, Reviews in Conservation, No. 9, 2009, pp 61-74.

Wright, J.A.and J.F. Hanlan, (1978), Poly (vinyl pyrrolidone) as an aid in Removal of Stains from Textile and Ceramic Materials, Journal of the International Institute for Conservation – Canadian Group, Ottawa, Vol 4, No 1, 1978, pp 32-36.