HYDROGEN MITIGATION IN SUBMERGED ARC WELDING

By
Steven Klimowicz
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Golden, Colorado

Date:______________

Signed:______________

Steven Klimowicz

Signed:______________

Dr. Stephen Liu

Thesis Advisor

Golden, Colorado

Date:______________

Signed:______________

Dr. Chester J. Van Tyne

Professor and Interim Head

Department of Metallurgical and Materials Engineering
ABSTRACT

With the role of hydrogen in weld metal well understood in its relation to cold cracking, there has been a push to produce welds with lower and lower diffusible hydrogen contents. The push for lower diffusible hydrogen contents has placed pressure on consumables manufactures to create consumables that can achieve the requirements for lower diffusible hydrogen content. Currently EM12K flux is produced so that it can achieve below 4 ml of diffusible hydrogen for every 100g of weld metal deposited (ml/100g) for submerged arc welding (SAW). The recent trend for industry is to preferentially achieve diffusible hydrogen contents below 3 ml/100g. Making it necessary to find a way to modify the flux to achieve a lower diffusible hydrogen content for the welds it produces. To achieve this goal a two phase plan was developed. The first phase was to characterize the entire welding system for hydrogen. Since the goal of the project is hydrogen mitigation, any amount of hydrogen that could be reduced is helpful and therefore must first be discovered. Sources of hydrogen may be found by analyzing the welding wire and base metal, as well as breaking the flux down into its components and production steps. The wire was analyzed for total hydrogen content as was the base metal. The flux and its components were analyzed using differential thermal analysis-simultaneous thermal analysis (DTA-STA) and later vacuum degassing for moisture content. The analysis of the wire showed that the copper coating on the wire was the largest contributor of hydrogen. There was lubricant present on the wire surface as well, but it did not contribute as much as the copper coating. It was found that a simple low temperature baking of the wire was enough to remove the lubricant and coating moisture. The base metal was found to have a similar total hydrogen content to that of the wire. The breakdown of the flux and production process for moisture content analysis revealed that the production process removes the moisture that is added by the water based binder. The second phase of the project was to modify the flux with fluoride additions to remove hydrogen from the arc while welding. The introduction of fluorine into the arc would lower the amount of hydrogen that may be absorbed as diffusible hydrogen by the weld metal. To select the fluorides a series of thermodynamic calculations were performed as well as simple tests to determine the fluorides behavior in a welding arc and flux. From these tests the following fluorides were selected to be used to be added to EM12K flux as oneweight percent additions: SrF$_2$, K$_2$TiF$_6$, K$_2$SiF$_6$, and LiF. Welds were then run with the experimental fluxes according to AWS A4.3 standard for diffusible hydrogen testing. From these tests it was found that none experimental fluxes were able to achieve a diffusible hydrogen content lower than the original EM12K flux. It was also found that fluoride reduction in a simple flux is a better predictor of fluoride effectiveness than decomposition temperature.
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CHAPTER 1: BACKGROUND

The goal of this Chapter is to provide background material so the objectives of the project are understood. The objective of this project and the research it entails is hydrogen mitigation in a submerged arc welding system. By mitigating hydrogen it is possible to reduce the diffusible hydrogen content of a weld. The system in consideration is for welding of HY-80 steels. The consumables used for this are a copper coated ER100-S1 wire and EM12K agglomerated flux. The project is split into two main research areas. The first is the characterization of the welding system. The second is fluoride additions to the flux. The material below is to provide information needed to understand how and why this research is being carried out.

1.1 Hydrogen in Weld Metal

Hydrogen in weld metal is not a new area of study. The effect of hydrogen in metal has been a topic of research for many years[1]. The detrimental effect of hydrogen in metals is the reason for this interest[2]. Atomic hydrogen is an interstitial element in the system of steels. In the body centered cubic structure of iron the interstitial sites are large enough that hydrogen is free to move unimpeded through the structure[3]. Therefore it is free to move to preferential sites around dislocations and crack tips. When hydrogen localizes around crack tips it induces a phenomenon called hydrogen enhanced localized plasticity. When hydrogen diffuses to the crack tip it stresses the lattice locally. Then when a stress is applied, since the lattice is already strained, the material fails in a brittle fashion at stresses lower than the ultimate tensile strength [4]. If enough hydrogen is present in the crystal lattice it can combine to reform

A.)

B.)

Figure 1.1 Hydrogen blisters. A.) Hydrogen blisters that formed close enough to the surface of the metal to be visible. B.) Hydrogen blisters that have been linked by cracks in a step-wise fashion [5].
molecular hydrogen. Since molecular hydrogen occupies a larger volume than atomic hydrogen it can create significant internal stresses. These stresses are enough to initiate cracks that cause voids known as blisters. If the hydrogen blister is close enough to the surface they can be viewed as shown in Figure 1.1 A. Since the blisters were originally formed from cracks it is likely that they will propagate cracks when a stress is applied to the material. If the hydrogen blisters are close enough the cracks can link the blisters and cause a premature failure as seen in Figure 1.1 B. The control of hydrogen in steels is rather important as it can prevent premature failures. The control of hydrogen is even more important in steel welds.

Before the effect of hydrogen in welds is covered it is important to discuss the different types of hydrogen that may be present in steel. There are three hydrogen categories when refereeing to hydrogen in steel. The first is diffusible hydrogen. The diffusible hydrogen is present as atomic hydrogen in the steel that is mobile at temperatures near room temperature. It may diffuse through the steel to a free surface or defect, hence the name diffusible. The second is residual hydrogen. This type of hydrogen is also referred to as trapped hydrogen. If one were to let all of the diffusible hydrogen to diffuse out of the steel the remaining hydrogen would be residual hydrogen. This hydrogen is not able to diffuse out of the sample without elevated temperatures. The hydrogen exists at trap sites in the steel. The traps sites in steel exist in many different forms. They can be at inclusion sites such as oxides, or at second phase particles such as carbides[6]. Grain boundaries and dislocations will also attract hydrogen and act as trap sites[7]. Additionally different phases may act as a hydrogen trap. In steels hydrogen is free to move through ferrite due to large interstitial sites. However in austenite the sites are smaller and the diffusion of hydrogen is lowered so much that it acts as a trap[8]. The effectiness of each of these trap sites is often rated by what temperature is needed to overcome the bond energy and release hydrogen.

The last term used is total hydrogen, and refers to all hydrogen in a steel at the time of testing. It may consist of both types of hydrogen, but since it was not possible to distinguish if diffusible hydrogen was present or not it must be termed total hydrogen until proven otherwise. In structural steel welding the type of hydrogen that is of the most concern is the diffusible hydrogen. This is the type of hydrogen that causes cracking in welds.

For welds to be susceptible to hydrogen cracking, otherwise known as cold or delayed cracking, it requires four things: hydrogen in the weld metal, stress, susceptible microstructure, and relatively low temperature [9]. Since the cracking is related to hydrogen, there must be hydrogen present to induce cracking. It must be diffusible hydrogen so that it can diffuse to preferential defects, such as crack tips. To promote crack growth a stress must be present. During welding there are stresses present due to thermal contractions[10]. These contractions induce a tensile stress on the weld that is required for crack
growth. There are many microstructures that can be obtained from steels. Martensite is the most susceptible to hydrogen cracking of all the microstructure, and is due to it being a hard and brittle microstructure. Additionally the formation of Martensite is accompanied by an increase in dislocation density that may form micro cracks[11], [12]. The temperature required for hydrogen cracking is relatively low, hence why it is called cold cracking. If the temperature is too high Martensite may not form, and the hydrogen may be able to diffuse away from defects. Since it does occur at low temperatures it may take some time for hydrogen to diffuse to preferential locations and initiate or promote crack growth. Since the cracks may not be formed immediately after welding and require time to form, hydrogen cracking is sometimes referred to as delayed cracking.

The location of hydrogen cracking in welding has also led it to be termed underbead cracking. The naming is due to the formation of cracks in the heat affected zone (HAZ) immediately adjacent to the weld bead. For bead on plate welding this location is under the bead. Figure 1.2 gives an example of hydrogen cracking in a fillet weld. There are two cracks that are present on either side of the crack. The cracks are preferentially located due to stress concentrations at the edges of the weld. There is a third crack present at the root of the weld near the gap between the plates being welded. The HAZ is the location of cracks due to the formation of Martensite and the diffusing of hydrogen to it from the weld metal due to solubility differences of hydrogen in Austenite and ferrite[13].

Figure 1.2 Hydrogen cracking in a fillet weld. There are three cracks present the HAZ of the weld. Magnified 4.5x [9].
There are ways of reducing the susceptibility of hydrogen cracking of a steel weld[14]. One way is to change the welding operation so that it no longer forms Martensite. Though generally changing a welding process is not desirable as it will generally lower productivity, or may form undesirable welds. The next method of reduction is to remove hydrogen. The removal of hydrogen may be done by removing hydrogen from consumables, by baking fluxes or storing in moisture tight packaging. Another method is to provide a post weld heat treatment to provide energy to overcome the preference of hydrogen to diffuse to defects in the weld[15]. This method removes the hydrogen as at an elevated temperature the time required to diffuse out of the steel is lowered.

However in a large production ventures the parts are not easily heat treatable or it may be cost prohibitive to post weld heat treat a long weld. This heat treatment may also cause distortion of the weld as a larger area is heated over time and the thermal contractions will be larger causing more distortion. Since it is unlikely that removing hydrogen from the weld after it is made is likely, it is more effective to remove hydrogen from ever entering the weld. For consumables manufacturers this is an area of interest. The lower a manufacture is able to get the diffusible hydrogen content in a weld with their consumables the more likely it is that their product will be used in projects that require strict limits on diffusible hydrogen contents.

1.2 Welding and Fluxes

To understand where the hydrogen can come from during welding, it is necessary to understand the welding system. Welding is a joining process widely utilized in metal systems. Steel and aluminum are the most common materials to be welded. Welding itself can be broken down into two types: arc welding and non-arc welding. Non-arc welding would include processes such as resistance welding, friction stir welding and laser welding. There is no requirement that these processes use electricity directly as the means of forming the bond, such as the case of laser welding and friction stir welding.

Arc based processes do use electricity as their main source of energy. It is used to ionize a column of gas to form a plasma and is termed the welding arc. Hence the name arc processes. Arc processes can be further broken down into two groups: flux based and non-flux processes. Non-flux processes will include such processes as gas tungsten arc welding (GTAW), gas metal arc welding (GMAW), and plasma arc welding. Non-flux processes utilize a shielding gas and an arc is established in this gas with either a non-consumable electrode or consumable welding wire. The shielding gas is used to protect the weld from oxygen. Flux based processes have a mixture of chemicals that provide protection for the weld and modify the weld properties. Flux processes include submerged arc welding (SAW), shielded metal arc welding (SMAW), and flux core arc welding (FCAW). The main difference between the flux based processes is where the flux is located during welding. Figure 1.3 gives a schematic for
both FCAW and SMAW. In FCAW it is seen that the flux is a loose powder that is placed inside the welding wire. For SMAW the flux is seen as an extruded coating on the outside of the welding rod. For SAW the flux is not present on or in the welding wire. Instead the flux is present as a blanket over the area to be welded. A schematic of SAW with possible sources of hydrogen highlighted is given in Figure 1.4. The name of SAW comes from the arc being submerged under a layer of flux. The fluxes used in all of the processes, while present in different forms and locations; perform the same duties for each type of welding.

![Figure 1.3 Schematics for flux based welding processes. A.) Formation of FCAW wire. Here a strip of metal is formed into a wire with flux inside. B.) SMAW process. Top half of image is cross section during welding an bottom is cross section of completed weld.](image)

The flux performs several duties during welding that include protecting the weld, alloying, morphology, detachability of slag and many others[16]. Each of these duties is carried out through careful formulation of the flux. Each ingredient will have an effect on the final properties of the flux. For example calcium ions are added to increase arc stability, and may come from calcium fluoride other additions[17]. Titanium dioxide is added to enhance the slag detachability[18][19] and may also promote the formation of acicular ferrite[20]. Manganese oxide has been observed to enhance the mechanical properties of the weld[21]. While these additions are made to improve a specific quality of the flux, it may have a second effect. Manganese oxide, calcium fluoride and titanium dioxide are known to decrease the viscosity of the flux[22].

Viscosity is an important property of the flux. If the viscosity is too low then the molten flux will be too fluid to cover the weld exposing it. If the viscosity is too high then the weld will not flow correctly. Additionally if the viscosity is too high then the flux will not allow for outgassing[14]. This
would hold in any gases including hydrogen and create a forced raise in the hydrogen content of a weld. Therefore it is necessary to create a proper viscosity of the flux that is viscous enough to cover the weld, yet fluid enough to allow for outgassing. This makes the proper formulation of a flux very important.

While flux formulation is important, the welding process itself is also important in determining how the flux will and should function. In multi-pass welding the slag detachability is of a larger concern than in a single pass. This is from wanting to eliminate slag inclusions in the weld. When multiple wire feeds are used in a single pool it is common to use different polarities for the wires. Polarity is one of the largest factors concerning flux performance during welding[23].

![Figure 1.4](image)

Figure 1.4 Schematic of SAW. The highlighted components are possible areas of hydrogen contribution during welding.

SAW, as was seen from Figure 1.4, has several possible sources of hydrogen. To form a complete and comprehensive study of hydrogen in welding the entire welding system needs to be analyzed. However some of the sources can be eliminated from the start. The welding flux is designed to provide a shielding gas for the weld. Therefore it should displace any atmosphere during welding and it should not be present to contribute any hydrogen to the weld. The base metal will also have a limited contribution. It will have hydrogen present as lubricants on the surface or as trapped hydrogen. Any diffusible hydrogen should be gone by time the metal is welded. Any remaining forms of hydrogen present as lubricant, or any other hydrogen containing surface contaminant, should be removed during weld prep. This means that the only contribution from the base metal should be the trapped hydrogen.
Therefore it can be assumed that the contribution from the base metal will be minimal, but it should still be quantified for a complete analysis of the welding system.

The welding wire is similar to the base metal in forms of hydrogen present, but it has an additional form beyond the trapped and lubricant hydrogen. This is the hydrogen present in the wire coating. The coating is deposited electrolytically so there may be some form of hydrogen present in the coating. The core wire used for the consumable should be limited to trapped hydrogen. The lubricant on the surface will be leftover from the drawing and packaging operations. The lubricant on the wire would be expected to be the largest contributor as it can vary from wire to wire and there is no ideal way to measure it. Additionally some form of oil may be beneficial on the wire to prevent corrosion from occurring on the wire. The last source of hydrogen is the flux.

Fluxes for SAW can come in three different forms: Fused, Bonded, and agglomerated [16]. These forms come from the different production methods. Fused fluxes are first dry mixed then melted in an electric furnace. Once molten the flux is then poured and cooled into a glass like product. This glass is then broken up and screened to the appropriate size. Bonded fluxes are dry mixed first then wet mixed with a binder. The wet mix is then pelletized and dried at a relatively low temperature. After drying the pellets are broken up and screened to size. Agglomerated fluxes are similar to bonded fluxes. They are dry mixed and then mixed with a binder for the wet mix. The difference is that the wet mix is then goes to an agglomerator where wet mix forms into small particles. These particles are then dried and screened. There is no mechanical breaking of the flux, it is formed directly into near final particle size. The EM12K flux that was used for this project was an agglomerated flux.

Binders for agglomerated fluxes are generally a silicate. The two main silicates used are potassium or sodium silicate[16]. The predominance of use of these silicates is their ease of use. They have little effect on the arc during welding or off putting fumes. They are easy to add to the dry mix and can be incrementally added without needing to keep an optimized ratio. They require no secondary reaction to from a hard bond and therefore are easily used to form agglomerated fluxes. The large drawback is that they require a high drying temperature and are water based.

Moisture in the flux and diffusible hydrogen has been linked together before. Previous work by Kiefer [24] has shown that in FCAW there is a distinct relationship between total hydrogen in the wire and the diffusible hydrogen content. Work has also been done with SMAW. Figure 1.5 is from the work of McKeown [25]. Here it is shown that as the moisture content of the flux coating is increased the diffusible hydrogen content is increase when compared against similar flux formulations. It is important to note that every flux type will have its own behavior related to moisture content and diffusible hydrogen. There is no universal equation or rule that applies to all fluxes that predicts what the diffusible
hydrogen content will be with a given moisture content. The lack of such an equation makes it necessary to characterize any flux that is being used to determine this behavior.

![Figure 1.5](image)

**Figure 1.5** Relationship between moisture that was re-absorbed by flux coatings on SMAW electrodes and the diffusible hydrogen content obtained by them [25].

Since it is known that there is hydrogen present in the welding system it is important to come up with a hydrogen management strategy. Hydrogen management can be broken down into four stages: eliminating hydrogen from materials, elimination of hydrogen from the arc plasma, elimination of hydrogen by forming barriers on weld metal droplets, and rendering hydrogen immobile by trapping [26]. The first goal of this project is to identify where hydrogen and exists and how much is there. The identification of the hydrogen sources helps to lead to hydrogen mitigation by identifying where it may be possible to remove hydrogen in the system and thus lowering the diffusible hydrogen content.

### 1.3 Fluorine Additions to Welding Fluxes

From the hydrogen management plan given in the previous section it was seen that there are several methods to reduce the diffusible hydrogen content of welds. Hydrogen trapping has been shown to be very effective in reducing the diffusible hydrogen content of welds. Work done by Park [27] has shown that additions of ferro-yttrium can reduce the diffusible hydrogen content of a weld below 1 ml/100g by introducing traps sites.

While trapping is an effective way of reducing the diffusible hydrogen content of a weld, as shown in Figure 1.6, the issue it brings up is that it raises the residual hydrogen content. The rise in the residual hydrogen content raises the issue of how long will the hydrogen trap last or hold the hydrogen. If the hydrogen is released it has the potential to cause the damage that it would have done if it was not
originally trapped. While the strategy of hydrogen elimination in the materials is a start, it may not be feasible to accomplish if the production methods are not flexible enough to accommodate any needed changes to reduce hydrogen contents. The concern with the flexibility of the system also applies to the establishing of barriers to eliminate hydrogen. If there is a welding system that is already in place that works, making changes to the flux or wire chemistries to may alter the system so that it no longer

![Image of Figure 1.6](image_url)

**Figure 1.6** Effect of rare earth metal additions to flux on diffusible hydrogen content. Note that as the diffusible hydrogen content is lowered the residual hydrogen content is increased [28].

performs as desired. With the choices limited it leaves the method of reduction for an existing system to elimination of hydrogen from the arc plasma, if it is not possible to eliminate hydrogen from materials.

To eliminate hydrogen from the arc plasma it is necessary to understand how it is possible to do so. There are several methods that have been shown to reduce the diffusible hydrogen content of welds through additions of compounds to the welding flux. In an attempt to dilute the hydrogen in an arc, additions of calcium carbonate and iron oxide can be added to the flux. These compounds will decompose and produce oxygen and carbon dioxide that can be further decomposed. These new gases will dilute the hydrogen present in the arc and lower the diffusible hydrogen content in an agglomerated flux system as shown in Figure 1.7. While these additions are useful in developing a low hydrogen flux, if the flux system is already developed further additions may change the weld properties or slag properties so that the flux system no longer performs as desired.
The change in behaviour is best observed by experiments done by Pokhodnya [28] with calcium fluoride and calcium oxide given in Figure 1.8. Calcium fluoride is used in fluxes as it has been shown to decrease the hydrogen content of a weld. When Calcium oxide is added it decreases the effectiveness of the calcium fluoride. As the minimal hydrogen content obtained in a molten flux is decreased as the as the amount of calcium oxide is increased. The addition of more calcium fluoride does overcome the effect of the calcium oxide in systems bearing calcium oxide, calcium fluoride and either alumina or rutile. However when the system contains silicon dioxide the addition of calcium oxide does not affect
the behavior of the fluoride. However the fluxes that were used are simple flux systems and the addition amounts of the calcium fluoride are rather large. Therefore it is necessary to find a different addition that can be made in smaller additions that can reduce diffusible hydrogen.

While calcium fluoride is used readily in fluxes, it has a limited impact on the diffusible hydrogen content. This is limited effectiveness is given in Figure 1.9. It is seen that in a weld that starts out near 10 ml/100g of diffusible hydrogen that calcium fluoride is able to remove 3 ml of diffusible hydrogen at an addition of 22 weight percent. The reduction is seen when the system has an abundance of hydrogen present in the system. When a welding consumable is only producing 4 ml/100g of diffusible hydrogen then it is unlikely that calcium fluoride will be very effective at removing any more hydrogen. From Figure 1.9 it is even possible that further additions of calcium fluoride may produce an increase in the diffusible hydrogen content.

The method that is being considered for the reduction of diffusible hydrogen is the reaction of fluorine with hydrogen in the arc to form hydrofluoric acid which is insoluble in the weld metal. This trend is established in Figure 1.10. Here it is seen that as the hydrofluoric acid in the arc increases that the diffusible hydrogen content is decreased. The amount of hydrofluoric formed is related to how much fluorine is dissociated from the flux. The amount of fluorine dissociation may be useful in identifying what fluorides will serve better at reducing the diffusible hydrogen content than others.

Figure 1.9 Effectiveness of calcium fluoride at managing diffusible hydrogen. Welds were made using SMAW [29].

![Graph showing effectiveness of calcium fluoride at managing diffusible hydrogen.](image-url)
One way to introduce fluorine into the arc is through introduction in a gas. There currently exists technology for GMAW to introduce fluorine into the shielding gas\cite{30}. This has also been adapted for SAW, by creating a special nozzle that can introduce a fluorine containing gas to the flux and welding arc area\cite{31}. While this method may provide fluorine directly to the arc it has drawbacks in that the weld setup must be modified. Additionally there is a concern with providing fluorine gas to the weld area for health and equipment longevity.

To raise the fluorine content in the arc fluorides may also be used. Currently there is no database that is available to select fluorides from for reduction of diffusible hydrogen. The research is still in the experimental stages, and effectiveness of fluorides is still being researched. There is current work that is done on fluorides that can help to determine what fluorides are currently being used and are effective in reducing diffusible hydrogen contents. Work done by Matsushita\cite{32} shows the relation of several fluorides and the calculated diffusible hydrogen content based on partial pressure of hydrogen in an arc. His results are shown in Figure 1.11. Of the several fluorides that were calculated for, the most promising at reducing the diffusible hydrogen content in FCAW welds were KF and MnF$_3$. However it must be noted that this information was calculated. Further work done by Matsushita showed that at five weight percent additions of the fluorides to FCAW wires that KF is much more effective than MnF$_3$. Further experimental work that has been carried out with selected fluorides by Pokhodnya\cite{33} is presented in Figure 1.12. Here the fluorides were added to FCAW wires at an addition that would result in similar fluorine ion contents in the flux. By keeping the fluorine constant it allows for the comparison of the fluorides by their ability to produce the fluorine ion. In contradiction to the work that was previously shown this experimental data shows that KF has one of the higher diffusible hydrogen contents.

Figure 1.10  Weld metal hydrogen relationship with fluorine in the flux \cite{14}.
Figure 1.11  Calculated diffusible hydrogen content for welds with various fluoride additions with increasing partial pressure of hydrogen in the arc [32].

Figure 1.12  Diffusible hydrogen contents for FCAW wires with various fluoride additions. Fluorides were added so that the fluorine ion content was consistent in the welding wires [33].
Complex fluorides, such as $\text{K}_2\text{SiF}_6$, have a better performance than binary fluorides. Furthering the work that has been present so far is the work of Murakami [34]. His work was done with additions of $\text{K}_2\text{TiF}_6$ and $\text{KBF}_4$ to FCAW wires and included analysis of an inclusion content study. His work compared to that of the previous authors on fluoride additions is given in Figure 1.13. Here it is seen that

![Figure 1.13](image)

Figure 1.13 Combined results of fluoride additions effects on diffusible hydrogen contents of welds made by FCAW [34].

the further additions of $\text{K}_2\text{TiF}_6$ do not have a large improvement over the results seen from Pokhodnya. However $\text{KBF}_4$ shows great potential at reducing the diffusible hydrogen content of welds. It is important to note that all of these additions were made at less than five weight percent. Therefore it may be possible to add these fluorides to an existing flux system without changing the properties. However it is important to note that all of these fluorides were added to FCAW wires and that there may be some differences between these results and those obtained for SAW.

Fluorides are only one of the possibilities for additions to reduce hydrogen. There are other fluoride containing compounds that exist. Of these compounds polytetrafluoroethylene (PTFE) is one that is of interest. It is a polymer that the individual mer consists of two carbons and four fluorines. There exists some welding consumables that currently use PTFE to achieve a lower diffusible hydrogen content[35]–[37]. While PTFE may be an ideal addition to reduce hydrogen it has some concerns attached to it. The addition of PTFE in FCAW wires is easily achieved. For a SAW flux it has two issues. The first is that as a polymer it has a low combustion temperature. Therefore it is likely that it
will not survive kiln treatments so it must be added after these steps of production. Second is that PTFE is known for its non-stick properties. This will make it difficult to adhere to a flux that is created. The last concern is that there are health issues associated with combusting polymers. With the concerns the compounds chosen for reduction with these experiments will be kept to fluorides.
CHAPTER 2: EXPERIMENTAL PROCEDURE

For a given welding system there exist many forms of hydrogen. In order to reduce the diffusible hydrogen content of a weld it is beneficial to know where and how much hydrogen exists in a system. Once the sources are known it is possible to reduce these sources. If reducing the sources is not possible, it is possible to make additions to a known system in small enough amounts that it does not change the system performance, yet will reduce the hydrogen content. The experimental procedure below describes the methods used to analyze a SAW system for hydrogen content. It then describes the methods of selection for additions of fluorides to the flux to try to reduce the diffusible hydrogen contents of the welds produced by them.

2.1 Flux Evaluation and Breakdown

All flux received for these experiments was from an commercial manufacturer and was EM12K flux. The flux is an agglomerated neutral flux. The composition of the EM12K flux is given in Table 2.1. Given the main ingredients the flux falls into the neutral flux category [16]. To determine where the moisture is in the flux it needs to be broken down into the individual components. This way if a single component is at fault for a large hydrogen contribution it may be reconsidered for the flux. For this analysis the individual components of the flux were also sent to CSM in addition to the flux. Additionally comparing the moisture content of the flux and the individual components will indicate whether or not there is any moisture pickup during production.

Table 2.1 – Composition of EM12K flux [38].

<table>
<thead>
<tr>
<th>Component</th>
<th>Al₂O₃</th>
<th>CaCO₃</th>
<th>CaO</th>
<th>Fluorides</th>
<th>MgO</th>
<th>Mn</th>
<th>MnO</th>
<th>Silicate</th>
<th>Si alloys</th>
<th>SiO₂</th>
<th>FeTiO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>15-20</td>
<td>5-10</td>
<td>2-5</td>
<td>20-30</td>
<td>30-40</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>5-10</td>
<td>1-5</td>
<td>2-5</td>
<td>1-2</td>
</tr>
</tbody>
</table>

To obtain the moisture content differential thermal analysis with simultaneous thermal analysis (DTA-STA) was used. An illustration of the DTA-STA is shown in Figure 2.1. This method uses thermocouples to measure the thermal experience of a sample that is located on a balance arm. This way any mass losses can be related to a thermal event if one occurred. The addition of the thermal event history is useful as water loss will not have a thermal event associated with it, while any decomposition reaction that may occur will. The machine has two thermocouples that are located directly beneath two crucibles. This way a reference may used to see further changes in a sample. The crucibles are located
inside a furnace chamber and are connected to a balance arm below the furnace. The furnace chamber is separate from the balance chamber, so it does damage the balance. Both chambers can be sealed for operation under a low vacuum, or with a gas flow. DTA-STA has been used successfully before for moisture content[39].

Figure 2.1  DTA-STA schematic. Furnace chamber with sample carrier is seen on the top half of the instrument. The bottom half of the instrument contains the balance arm that is attached to the sample arm.

For testing of the flux and its components alumina crucibles were used and one was kept empty as the reference to record the furnace chamber temperature. The furnace was run from room temperature to 900°C at a rate of 30 K/min. Argon was used as the cover gas and the chambers were purged twice to remove any air. Before testing began the furnace was calibrated with two empty crucibles used for the specified ramp rate and temperature range. The mass profile obtained from the calibration run is used to remove any artifacts during testing produced by the density changes that occur in the cover gas during heating.

For testing the flux and its individual components were run with a sample size that filled half the crucible as they were all in powder or small pellet form. This was to prevent the sample from trapping air in the crucible and causing the sample to “blowout” while the chamber pressure lowered to a low vacuum. The sample size was weighed before testing and ranged in size from 100 mg to 400 mg. While it is stated
that all of the flux components underwent analysis for moisture content it is noted that the binder used is not included.

The binder was not analyzed due to the binder being a liquid silicate. While it may be possible to do a moisture analysis of a liquid binder with DTA-STA, due to the intumescent nature of the silicate binder it is not possible [40]. Since the comparison of the components and the flux is a before and after picture that may include the effects of the binder it is necessary to expand the range of moisture content testing of the flux. To get a complete picture of what the binder might contribute to the moisture content the flux production cycle must be analyzed for moisture content.

The production process is shown in Figure 2.2 and consists of the following main steps: wet mixing, agglomerating, low temperature kiln, high temperature kiln, cooling table and packaging. To analyze the process samples were taken for analysis after the agglomerating, low and high temperature kilns, and the cooling table. The flux received previously would serve as the packaging step and the components would serve as the step before wet mixing. Since the flux goes straight from wet mixing to agglomerating the samples taken for these steps would be the same, and thus only one was chosen for use. The samples taken from these steps were also sent to CSM for analysis using DTA-STA. The procedure for these samples followed the previously described procedure for the flux components.

![Diagram](image)

**Figure 2.2** Flux production process for agglomerated flux. First dry ingredients are combined and added to a mixer. Then wet ingredients such as the binder are added and everything is mixed together. The wet flux then drops onto a disc agglomerator. It then passes through a low and then high temperature kiln. After the kilns it passes through a fluidized bed cooler and is then packaged.
2.2 Wire and Base Metal Evaluation

The wire used in the given welding system is a low carbon copper coated wire. It is important to determine the hydrogen in the wire as it may contribute to diffusible hydrogen. In addition to the wire the base metal may also contribute to the diffusible hydrogen content. The base metal consists of HY-80 steel that is common in shipbuilding.

2.2.1 Wire

While it is known that the welding flux is the main provider of hydrogen during welding, it is possible that the wire can contribute to the total amount of hydrogen. To determine the hydrogen in the wire, the wire was tested for its hydrogen content and was also tested on how to remove the hydrogen from the wire if there was any. To analyze the hydrogen content of the wire a LECO RH-404 hydrogen determinator was used, and will be referenced as hydrogen determinator, that measures the total hydrogen in a sample. The machine is seen in Figure 2.3. It consists of a furnace unit where a sample is melted in a graphite crucible. Any gas evolved during melting is then carried by an argon gas flow to the determinator. Here a gas chromatography (GC) coil separates the hydrogen from other gases. Then the separated gases flow into a detector where the amount of hydrogen is calculated. The amount of hydrogen is calculated from a calibration that is set from standards that can be run. This method of analysis is a destructive testing method as it melts a sample in a crucible to release any hydrogen in the sample.

Figure 2.3 LECO machine used for all total hydrogen measurements. The RH-404 hydrogen determinator is the unit on the left, which contains the detector and GC coil. The unit on the right is the EF-400 electrode furnace, where the sample is melted in a crucible.
The wire that was used for this analysis was a copper coated welding wire classified as ER100-S1. Three 50 pound spools of wire were received at CSM, two of which were 1/8 inch diameter and the remaining spool was 5/32 inch diameter wire. The 5/32 inch diameter wire shall be renamed “wire 1” and the 1/8 inch diameter wires will be renamed “wire 2” and “wire 3” for simplicity. To determine where the hydrogen may be coming from in the wire it is necessary to break the wire itself down. The wire may be thought of to consist of three main parts: the core wire, the copper coating, and a residual lubricant layer from processing. While it is not straightforward to separate each of these parts and measure them. It is relatively easy to subtract the effect of each part from the whole.

For samples the wires were cut into one gram segments, as required by the hydrogen determinator, which easily fit into the crucibles. Multiple samples were taken from a length of wire from each coil. Therefore while the sample size may seem small it is still representative of the whole. While handling the wires gloves were worn to prevent any contamination. Testing started with the wires in the as received condition. Then to remove the effect of any residual lubrication on the surface the wires were ultrasonically washed in acetone. The difference between the as received and washed wires was assumed to be any lubricant or other contamination from processing the wires.

To remove the effect of the copper coating and get the core wire hydrogen content the copper coating was removed. The removal of the coating was achieved by manually grinding a long segment of wire with grit paper. Then samples were cut from the middle section of the wire to remove the possibility of any residual copper that might remain in the original cut ends of the wire. The samples were then washed in acetone to remove any copper debris and lubricant/contamination from cutting and grinding. The samples were then run in the hydrogen determinator. The difference between the washed wires and the ground wires is assumed to be from the copper coating. This way all of the effects of the parts of the wire may be separated easily though physically they may not easily be separated.

Testing using the hydrogen determinator was carried out using the following process. The machine was turned on and the argon gas flow was allowed to run for at least half an hour before any testing occurred. After the half hour a series of 1.7 ppm hydrogen content standards were run. The standards were used to calibrate the machine for use. A correction value was obtained from the standards to calibrate the machine for the range of hydrogen that may be seen in the samples. After the machine was calibrated the wire samples were run. Each wire was run with a set of at least three samples. Each wire was run one sample set at a time. After each set of a wire a standard was run to ensure the machine was still within calibration.

It was assumed that there was going to be some amount of hydrogen found in the wires and that it may be possible to lower that amount. Since the goal of the project is hydrogen mitigation any amount of hydrogen that may be removed could be beneficial. To achieve this removal, the wires were chosen to be
baked. Since diffusible hydrogen should be gone from the wire by time of reception the remaining source is a form of trapped hydrogen. To release trapped hydrogen from a high bond energy site a temperature above 400°C must be used [27]. While the wire is small in diameter it is assumed that any industry would do a bulk heat treatment of the wire and this would increase hold times in a furnace. The following was the initial baking schedules for the wire: one hr at 450°C, and two hrs at 450°C. Additionally a higher temperature bake was used at 650°C for one hr to try to further drive out any hydrogen in the wire. Since the baking was done in an open air furnace there was a concern that the copper coating would oxidize so an additional low temperature bake was also included. This low temperature bake was carried out at 200°C for one hr. After baking the wires were prepared and tested in the manner that was previously laid out for the hydrogen determinator.

2.2.2 Base Metal

The specific focus of this type of welding is on HY 80 steels. HY 80 steel is an HSLA steel that has a minimum yield strength of 80 ksi [41]. The testing of the base metal was very similar to that of the method of evaluation for the wire with the use of the hydrogen determinator. Instead of a spool of wire the base metal was supplied in 1 x ½ inch bar stock cut to lengths of 3 1/8 inch. To get a sample down to a size for analysis a sample coupon was necessary to be made. The creation of this sample was achieved by sectioning the coupon from the bar using an abrasive saw. After sectioning the coupons are still too large for analysis so they must be ground down manually till they are able to fit in the analysis crucible. Once the coupon would fit in the crucible it was further ground until the weight of the coupon was approximately one gram. The coupons were then washed with acetone and further handling of the coupons was done with gloves to prevent contamination. There is no need to test in the as received or other conditions because if proper weld preparation occurs any surface contaminants should be removed. For analysis the hydrogen determinator was used. The machine was calibrated before testing with 1.7 ppm standards and high temperature graphite crucibles were used.

2.3 Fluoride Refinement

One of the goals of this project was to make modifications to the welding system to reduce the diffusible hydrogen content it can obtain. Since large changes to the system may not be possible, small additions of fluorides were to be added instead. To the select the fluorides several selection methods were used. The methods and experiments used to select the fluorides are described in this section.

2.3.1 Thermodynamic Calculations

With the selected method of hydrogen reduction being fluoride additions there must be some method of selection for the fluorides. There are a large number of fluorides that are present in the world
and some may not be able to be used due to undesirable characteristics or reactions that may occur during production of a welding flux. When the entire realm of fluorides is to be considered for use there are some simple exclusions that can be made before the start of the experiments. The simple exclusions would remove any fluorides that exist as a gas or liquid at room temperature. Additionally any fluorides that will present significant health risks can be removed. While most all fluorides present some risk in their use there are degrees of risk that cannot be tolerated and therefore those fluorides are not looked into.

With these fluorides removed the remaining amount of possible fluorides is still rather large and it is possible that some of the fluorides will have unwanted reactions during production. So in order to eliminate these fluorides without having to test every one possible thermodynamic calculations were carried out. For these calculations a reaction had to be defined. There are two reactions that would be considered an issue during production or during welding. These reactions are the decomposition of the fluoride and the reaction of the fluoride with water. Both of these reactions would be undesirable during production as they would produce fluorine gas that will damage equipment and pose as a health hazard. Also if the fluoride is not able to decompose during welding then it will not be effective during welding.

The first reaction that will be looked into is the decomposition of the fluoride. For welding applications it is important to know when a fluoride will decompose from the compound into its components with fluorine gas produced that can further breakdown. This reaction is given in Equation 2.1 and CaF$_2$ is given as an example. Here CaF$_2$ breaks down into strontium and fluorine gas.

\[ MF_2 \rightarrow M + F_2 \rightarrow M + 2F \]  
\[ CaF_2 \rightarrow Ca + F_2 \rightarrow Ca + 2F \]

The fluoride gas can then further decompose to provide two fluorine atoms for hydrogen removal. There are two decompositions presented from this Equation, but the one of interest is the initial fluoride decomposition, as that will produce the fluorine. Since the kilns will be heating the fluoride the temperature at which the fluoride decomposes is of interest. To find this temperature Equation 2.2 is used. Equation 2.2 is the equation for the free energy of a system [42]. $\Delta G$ is the change in free energy of a system, $\Delta H$ is the change in enthalpy, $\Delta S$ is the change in entropy and $T$ is the temperature of the system. It is assumed that the decomposition reaction will proceed spontaneously when the free energy of the system decreases. Since the equation gives the change in free energy all that is needed to be found is

\[ \Delta G = \Delta H - T \Delta S \]  
\[ 2.2 \]
the transition point when the change in free energy goes from positive to negative, or rather when the free energy change in the system is zero. So if ΔG is set to zero and the equation is solved for T, as shown in Equation 2.3, then when values are known for the remaining variables the transition temperature, or decomposition temperature rather, can be obtained.

\[ T = \frac{\Delta H}{\Delta S} \]  

\[ \Delta G_{\text{reaction}} = (\Delta H_{\text{products}} - \Delta H_{\text{reactants}}) - T(\Delta S_{\text{products}} - \Delta S_{\text{reactants}}) \]  

Since the use of these equations is for a reaction the variables themselves are made up of changes between states. Therefore the variables shall be the energy changes defined as the products minus the reactants when using values. Equation 2.4 shows Equation 2.2 fleshed out with the reaction inputs. To carry out these calculations several thermodynamic values must be known for the reactants and products, such as the enthalpy and entropy. For this calculation thermodynamic values were gathered for as many fluorides that had the data existing, the values were obtained from the CRC Handbook of Chemistry and Physics [43] and NIST WebBook [44]. When the values are input into Equation 2.3 then the decomposition temperature can be obtained.

The second reaction that is of interest with the fluorides during production is that of the interaction of the fluoride and water. The reaction is given in Equation 2.5 and again CaF₂ is given as an example. During production of welding fluxes a silicate binder containing water is used. The wet flux is then heated to try to remove the moisture in the flux. While the flux is heated it is possible that the fluoride will react with the water present while at elevated temperatures. If it does react then the reaction products will be a metal oxide and hydrofluoric acid (HF). The creation of HF during production of the flux again poses a hazard to the machinery and the employees. Therefore it is important to remove any fluoride that will react with water at a temperature below that of the high temperature kiln, or 705°C. Additionally if the fluoride reacts in the kiln then it is effectively removed from the flux. If the fluoride is removed then it is not present during welding to remove hydrogen.

Again the number of possible fluorides is too large to carry out experiments for this and the inherit risks of this reaction make calculating the reaction temperature the best method of elimination. To
calculate the reaction temperature it follows the same procedure that was laid out for the previous
decomposition temperature calculations. Except that the water is included in the reactants and the
products change to HF and a metal oxide. To eliminate fluorides from the list of use it will have a
calculated reaction temperature below that of the high temperature kiln.

2.3.2 Fluoride Decomposition in an Arc

While thermodynamic calculations help to filter some of the fluorides out. The reactions that
they are used to predict for may occur at different rates. This means that using the decomposition
temperature as a prediction method of fluoride effectiveness may not be truly effective. The calculation
also does not predict the ease of decomposition. CaF$_2$ is known to have limited dissociation in an arc,
something that the simple equations do not predict. To predict the behavior of a fluoride a simple test was
developed. The test would help to predict the behavior of a fluoride in an arc by placing the fluoride in an
arc. Therefore by a mass balance the decomposition of a fluoride in an arc can be observed.

For this mass balance it is assumed that all mass loss during the exposure to the arc is from the
loss of fluorine from the decomposition of the fluoride. Since all of the fluorides that were used for this
study came in powdered form it was necessary to safely convert them to a form that would not be blown
around during exposure to an arc. The conversion was accomplished by using sodium silicate as a binder.
Initially an equal amount of binder was used for a specified weight of fluoride; however the equal amount
of binder produced some unworkable fluoride mixtures due to too much or too little binder. So instead
binder was added to each fluoride until a pliable mixture was formed. It is assumed that the amount of
binder is consistent for each volume of fluoride and does not impact the results of the test.

Once a pliable mixture was achieved with the fluoride it was formed into small pucks. The pucks were
then baked at 200°C for two hours. After baking they were allowed to cool and then stored in sealed
bags. For testing each fluoride had four pucks tested. Each puck was weighed prior to testing and placed
in a weighed steel crucible. The crucible was cleaned and weighed before every test. All handling was
done while wearing gloves or with tongs to minimize contamination. Once weighing was completed a
crucible was placed in a button melter. The button melter used is shown in Figure 2.4. The setup
consisted of two water cooled brass flanges with a glass globe between them. The bottom flange had the
gas inlet and a removable copper bottom that the crucible was placed on. The top flange contained the
gas outlet and a sealed PTFE moveable ball pass through that held the welding torch. The torch consisted
of a brass rod with a tungsten rod that was inserted in the end and held by a set screw. To prevent any
damage to the copper bottom from the fluoride the steel crucible was chosen as a cheap alternative that
could be readily replaced.
For testing the crucible was placed in the button melter and the cover gas was allowed to flow for at least one minute to remove any air in the chamber. The cover gas chosen for the experiments was argon. During this time the chamber was inspected for any leaks and coolant flow was also checked. After the gas flow time was sufficient the arc was struck. The arc was struck on the side of the crucible and then passed over the fluoride puck. The arc was run over the fluoride for five seconds and then extinguished. The welding current used was 150 A. After the arc was extinguished the cover gas was allowed to run for several minutes to remove any gases produced and to allow for some cooling of the crucible. The outgas of the button melter was bubbled through water and then vented directly to the lab fume collection. After the chamber was sufficiently vented the crucible was removed and allowed to further cool. Once it was cool the crucible with flux was weighed and recorded. This process was carried for the following fluorides: CaF$_2$, NaF, SrF$_2$, K$_3$AlF$_6$, K$_2$TiF$_6$, MgF$_2$, KBF$_4$, Na$_2$TiF$_6$, Na$_2$SiF$_6$, K$_2$SiF$_6$, and KF.

### 2.3.3 Fluoride Decomposition in a simple Flux

The assumptions made in Section 2.3.2 were rather large. That any mass loss while a fluoride was exposed to an arc may not hold. Additionally it does nothing to help predict the behavior of the
fluoride in a flux system. In a flux system there are several other components present that may react, inhibit or promote the decomposition of the fluoride. Since a fluoride is likely to be used in a flux system for hydrogen reduction it is useful to try to replicate this interaction.

To achieve this, a simple test was developed to mimic the conditions that would be seen during welding for the fluorides in a flux system. The test would consist of a flux that was made with a specific fluoride and would then be exposed to an arc. This way the interactions with the components of the flux could be factored in. Additionally a different characterization method must be used. To determine if the fluoride had decomposed x-ray diffraction (XRD) would be used to analyze the fluxes. Using XRD a before and after scan of the fluxes can determine the degree of fluoride decomposed.

Instead of a complex flux system, the three main components of the EM12K flux were used in addition to the fluoride. From Table 2.1 it is seen that the three main components are CaF$_2$, Al$_2$O$_3$, and MgO. Since the behavior of a specific fluoride is the goal of this study CaF$_2$ is dropped and CaSiO$_3$ is used instead, so that only one fluoride exists in the system. The simple flux was made with the following composition: 5g Al$_2$O$_3$, 5g CaSiO$_3$, 12g MgO, 8g fluoride. The large amount of fluoride present in this simple system was chosen so that the behavior of the fluoride could be observed. Smaller additions may not be able to be fully analyzed.

All components existed as free flowing powders and were dry mixed after being weighed out. Then the components were mixed with sodium silicate as the binder. Enough silicate was added to form a pliable mixture. The amount of binder could not be held exactly constant as the different volumes of fluorides sometimes resulted in unworkable fluxes. Therefore it is necessary to assume that the binder added to all fluxes is consistent and will not affect the test. The mixture was then formed into pellets and baked at 200°C for two hours. After baking the pellets were allowed to cool and were stored in sealed bags until further testing when all fluxes were made.

Once all the fluxes were made they were tested one at a time. A pellet of flux was weighed and placed in a weighed steel crucible. Each crucible was cleaned and weighed before each test. The process was repeated for four pellets of flux. All handling was done while wearing gloves or with tongs to prevent contamination. After weighing, the filled crucible was loaded into the button melter. The button melter was previously shown in Figure 2.4. Due to the inherit corrosive nature of fluorides and the debris produced by the flux a steel crucible was used instead placing the flux on the copper platform of the button melter. Once a crucible was loaded into the button melter the argon cover gas was allowed to flow for at least one minute to clear the chamber of any atmospheric gases. During this time period the chamber was inspected for leaks and that coolant was flowing through the setup. Once the chamber was evacuated of air the arc was struck.
The arc was initiated on the side of the crucible and then run over the flux pellet insuring that all surface areas present were exposed to the arc. The flux was run under the arc for five seconds and then the arc was extinguished. The welding current used for was 150A. After the arc was extinguished the chamber was allowed to vent with the cover gas for several minutes to remove any gases produced and allow for some cooling of the crucible. After the chamber was sufficiently vented the cover gas was shut off and the chamber was opened and the crucible was removed and a new test was started. After all four flux pellets were run and cooled in open air the crucible with the exposed flux was weighed. After each crucible was weighed the flux was removed and collected. The collected flux was then stored until all of the fluxes had been exposed to the arc.

Once all of the fluxes had been exposed to the arc they were then milled into a powder. The milling was accomplished using the puck mill shown in Figure 2.5. The mill consists of a chamber with a steel puck that is free to move. The chamber is then rotated in a circular orbit that causes the puck to run against the inside of the chamber. Any flux caught in the path of the puck will be crushed and reduced in size. Each flux was run in the puck mill until it was reduced to a fine powder and then stored. In between each flux the puck mill vessel and pucks were cleaned to prevent cross contamination. Additionally unexposed pellets of flux were milled to use as a reference. The milled powders were then run in XRD for characterization. The powders were placed in an aluminum powder mount with a glass backing slide. Since it was unknown what might have formed in the reacted fluxes a full scan was performed on all samples. The analysis was done using copper radiation and the following settings: 10-150° 20 scan range, 0.004 step size, and 3.175 seconds scan time per step. The resulting profiles were then analyzed for the fluorides. This process was carried out for the following fluorides: CaF$_2$, K$_3$AlF$_6$, KF, SrF$_2$, KBF$_4$, K$_2$TiF$_6$, K$_2$SiF$_6$, and Na$_2$TiF$_6$.  

![Figure 2.5](image1.png)

A.) Puck mill used to convert fluxes to powders.  A.) Puck mill with top open and safety bar in place.  B.) Milling vessels with tops off and pucks inside
2.4 Diffusible Hydrogen Content of Experimental Fluxes

All fluxes used for this research were provided by a commercial manufacturer. From the process presented in Section 2.3 and the results in Section 3.3 the following fluorides were used to create experimental fluxes: \( K_2TiF_6 \), \( K_2SiF_6 \), \( SrF_2 \) and \( LiF \). All of these fluorides were added as a one weight percent addition to a small batch produced EM12K Flux. The smaller addition amount was done in hopes that the fluoride would be able to reduce hydrogen without causing large changes in the flux behavior. Additionally a batch of EM12K flux with no fluoride addition was produced using the same small batch method to be used as a control. A test was also conducted using EM12K flux that was produced industrially. All diffusible hydrogen testing done at CSM was done in accordance to the AWS A4.3 standard [45]. AWS 4.3 allows for the evaluation of the diffusible hydrogen either by mercury displacement or gas chromatography. The gas chromatography setup at CSM was being redesigned at the time of testing so all testing was done using mercury displacement. The method presented here is only a brief overview of the process.

Test sample pieces were made of ASTM A36 steel. Each 3 1/8 inch long piece was cut from a 1 x ½ inch bar. The pieces were heat treated at 550°C in an open air furnace for no less than an hour after an hour in the furnace for temperature equalization. After heat treatment the pieces were dry shot blasted to remove any oxide. After shot blasting the pieces were stamped with an identification code and weighed to the nearest 0.01 grams. The pieces were then stored until testing occurred.

Before testing the pieces were washed with acetone and any handling of the pieces after the washing was done wearing gloves to prevent contamination. For testing three pieces (start tab, a weld specimen, and a run off tab) were placed in a copper clamp fixture with copper foil. Experimental flux was then placed on top of the sample pieces. The fluxes were kept in a sealed container with desiccant packs to minimize moisture exposure. For testing the ideal welding conditions were 550 amps and 27 volts. However due to the limited amount of the fluxes received it was not possible to calibrate the welder to the behavior of each flux, also the fluoride additions are ideally not changing the slag properties of the flux. Therefore the welder was calibrated for the unmodified EM12K flux. The settings used for all welds were 27 volts with a wire feed speed of 41 inches per minute and a travel speed of 16 inches per minute. All weld settings were monitored for relation to ideal weld settings during the tests.

After a weld was completed the weld piece was vigorously quenched in an ice water bath and then placed in a liquid nitrogen bath. After the weld piece was in the liquid nitrogen bath for at least two minutes the piece was removed and clamped to a table for cleaning. Cleaning was done using a wire wheel on an angle grinder to remove any slag that remained on the surface. The weld piece may only be removed from the bath for less than a minute. So if all the slag was not removed in the first attempt the piece was returned to the bath for two minutes and the process was completed until all slag was removed
from the surface. After cleaning was completed the weld was measured for compliance with AWS 4.3 and if it fulfilled the requirements the end tabs were broken off and the middle section was returned to the bath. This process was repeated three more times for a set of four weld specimens.

The weld specimens were then transported to the mercury displacement setup in the liquid nitrogen bath. For the displacement tests, eudiometer tubes were used as outlined in AWS 4.3. The tubes were resealed with vacuum grease on the Teflon stopcocks and were leak tested before use. For the displacement tests the weld specimen was warmed in a water bath till the ice layer that formed was melted. The specimen was then dried with compressed air and placed in a horizontal tube on a magnet with the valve open and connected to a line to a vacuum pump. The magnet is there to hold the specimen in the tube when it was righted to be placed in a container filled with mercury. After the tube is placed in the mercury the valve was closed and the vacuum pump was turned on. The tube was evacuated of air by turning the valve till the mercury filled half the graduated section and the valve was closed.

It is necessary to remove any air bubbles that may have remained at the corners of the specimen by gently bouncing the tube on the bottom of the container. The bouncing of the tube is done until air bubbles no longer form around the specimen and rise out of the mercury. The valve was then reopened and the tube was fully evacuated of air. The valve was then closed and the tube removed. The process was repeated for the remaining weld specimens.

The mercury is inside a water bath that was held at 50°C for three days. The test setup is shown in Figure 2.6. Here the eudiometers are shown in the mercury containers. The containers are inside a controlled temperature water bath with a thermometer on the side for reference. For exact measurements and times required for the tests to be carried the reader is directed to AWS A4.3 [45]. After the specimen was held in the tube for three days the hydrogen collected was measured.

The amount of hydrogen is recorded to the nearest 0.02 ml. Then the head of the mercury is recorded to the nearest 0.2 mm. This head is the height difference between the mercury in the jar and the height of the mercury in the eudiometer tube. The air pressure and air temperature is also recorded. Since the hydrogen in the eudiometer is under pressure it is necessary to convert it to STP, standard temperature and pressure, conditions (0°C, 760 mm Hg). For this Equation 2.6 is used, where H is the head of mercury, P is air pressure, T is air temperature, V is volume of mercury collected, and VH is the corrected volume of hydrogen. Since the units of diffusible weld hydrogen are expressed as ml/100g there is one final conversion. The mass of the weld sample must be taken to the nearest 0.1 g.
Figure 2.6  Mercury displacement setup at CSM. Eudiometer tubes placed in a container of mercury. The assembly is placed in a controlled temperature water bath. The testing takes place in a fume hood to remove any mercury vapor that is produced.

Then the difference between the starting weight of the tab and the end weight is weld metal deposited. The corrected volume of hydrogen is divided by the weight of the weld deposit and multiplied by 100 and will convert the units to ml/100g. All four tests are then averaged and the result is the amount of diffusible hydrogen for the weld. In the event that a eudiometer tube leaks one, and only one, test result may be discarded and the remaining results are averaged. This procedure was followed for all five experimental fluxes and one test was performed with industrially produced flux as a further reference.

\[ VH = \frac{273}{(273 + T)} \times \left( P - \frac{H \times V}{760} \right) \]  

2.6
CHAPTER 3: RESULTS AND DISCUSSIONS

This chapter presents the results of all the experiments that were outlined in the previous chapter. It also presents several follow up experiments that were conducted to further the understanding of some of the results obtained from the original experiments. An attempt is made to explain some of the behaviors and trends that were observed.

3.1 Flux Evaluation and Breakdown

The first set of tests was done to evaluate the moisture content of the flux ingredients using DTA-STa. The results of these tests are given as Figure 3.1 – Figure 3.10. In each of these figures the results are presented as a thermogravimetric (TG) and differential scanning calorimetry curve (DSC). The TG results give the mass of the sample as a function of temperature. Here any mass loss can be related to temperature. The DSC curve is the temperature difference between the thermocouples. If any reaction occurs it will appear as a spike on the profile. The slow loss over the test, as seen in Figure 3.2, would indicate a loss of moisture that was absorbed. Step-like losses like those in Figure 3.1 would be indicative of adsorbed moisture. Once the bond can be overcome with thermal energy the moisture can leave at that point and a large mass loss occurs. Only two flux components had large spikes seen during the scans and these correlated to reactions. Calcium carbonate had a spike that correlated to its thermal decomposition. The decomposition temperature for calcium carbonate is generally agreed to be around 925°C. The reaction seen from this experiment occurs around 830°C, seen in Figure 3.9 B. Even though the reaction occurs nearly 100°C lower than what is expected it is believed that the decomposition reaction was indeed occurring. Calcium carbonate can have varying kinetics of decomposition and depending on the conditions of an experiment decomposition temperatures as low as 635°C have been observed [46].

The other flux ingredient to see a large reaction spike was lithium carbonate, seen in Figure 3.8 B. The lithium carbonate did not decompose, but rather it reacted with the alumina crucible once it neared its melting point of 725°C. The reaction caused a release of carbon dioxide and the formation of lithium aluminate. The reaction is given as Equation 3.1

\[ \text{Li}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CO}_2 + 2\text{LiAlO}_2 \]  

3.1
Figure 3.1  DTA-STA results for magnesium oxide. A.) TG curve for the sample as a function of temperature. B.) DSC curve for the sample as a function of temperature.
Figure 3.2  DTA-STA results for manganese oxide.  A.) TG curve for the sample as a function of temperature.  B.) DSC curve for the sample as a function of temperature.
Figure 3.3  DTA-STA results for calcium fluoride. A.) TG curve for the sample as a function of temperature.  B.) DSC curve for the sample as a function of temperature.
Figure 3.4 DTA-STA results for calcium silicate. A.) TG curve for the sample as a function of temperature. B.) DSC curve for the sample as a function of temperature.
Figure 3.5  DTA-ST A results for calcium silicide. A.) TG curve for the sample as a function of temperature. B.) DSC curve for the sample as a function of temperature.
Figure 3.6  DTA-STA results for ilmenite (FeTiO$_3$). A.) TG curve for the sample as a function of temperature. B.) DSC curve for the sample as a function of temperature.
Figure 3.7 DTA-STA results for aluminum oxide. A.) TG curve for the sample as a function of temperature. B.) DSC curve for the sample as a function of temperature.
Figure 3.8  DTA-STA results for lithium carbonate.  A.) TG curve for the sample as a function of temperature.  B.) DSC curve for the sample as a function of temperature.
Figure 3.9  DTA-STA results for calcium carbonate.  A.) TG curve for the sample as a function of temperature.  B.) DSC curve for the sample as a function of temperature.
Figure 3.10  DTA-STA results for EM12K flux.  A.) TG curve for the sample as a function of temperature.  B.) DSC curve for the sample as a function of temperature.
components any mass loss up to the reactions is attributed to moisture. The remainder of the components did not have any noticeable DSC reaction spikes. Therefore it was assumed that all mass loss was due to moisture.

The step like mass losses seen in the TG curves was explained as the different types of moisture. Adsorbed moisture will form a weak chemical bond that will break at a certain temperature and cause a sharp mass loss. The sharp drop is from simultaneous release of water. Absorbed water will be lost over time and will create a shallow slope. The multiple steps were understood as different bond energies for water and absorbed water that was shielded by the mass of the sample. However the actual cause of these step like losses may not actually have been water loss. While these slope trends will occur with moisture loss, they will occur at lower temperatures near the boiling point of water and slightly above [47]. It may be possible to have water loss at higher temperatures, but these would be in the form of water of crystallization, which none of the components are believed to contain.

In the cases where no clear reactions showed in the DSC scans, the mass losses could still be related to reactions with the crucible that are small enough to go undetected by the thermocouples. As the mass losses are very small compared to the mass of the sample, they do not produce enough energy to affect the thermocouple. A test was performed using another method to rectify this data and will be discussed later in this section.

To determine the moisture content of a component the mass loss over the test, or up to a reaction, was given as the moisture in the component. The moisture content analysis for all components and four containers of flux and the data collected is given in Table 3.1. The results show that none of the flux ingredients had above one weight percent moisture. A majority of the components had less than half of a percent of moisture by weight. Even though none of the individual components contained a large amount of moisture present it was still important to evaluate the production process and if the high temperature kiln is effective at removing moisture. From the scans it was possible to estimate the moisture removed by the high temperature kiln. By taking only the moisture lost up to 705°C the effectiveness of

<table>
<thead>
<tr>
<th>Component</th>
<th>Flux (avg.)</th>
<th>CaSiO₃</th>
<th>Li₂CO₃</th>
<th>MnO</th>
<th>CaF₂</th>
<th>MgO</th>
<th>FeTiO₃</th>
<th>CaSi₂</th>
<th>Al₂O₃</th>
<th>CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample mass (mg)</td>
<td>267.4</td>
<td>186.3</td>
<td>110.8</td>
<td>270</td>
<td>433.9</td>
<td>325.8</td>
<td>601</td>
<td>309</td>
<td>355.3</td>
<td>204.4</td>
</tr>
<tr>
<td>Mass loss (mg)</td>
<td>2.0</td>
<td>1.1</td>
<td>0.63</td>
<td>1.13</td>
<td>1.53</td>
<td>0.77</td>
<td>1.17</td>
<td>0.44</td>
<td>1.95</td>
<td>0.06</td>
</tr>
<tr>
<td>Moisture content (wt%)</td>
<td>0.76</td>
<td>0.59</td>
<td>0.57</td>
<td>0.42</td>
<td>0.35</td>
<td>0.24</td>
<td>0.19</td>
<td>0.14</td>
<td>0.55</td>
<td>0.03</td>
</tr>
</tbody>
</table>
the kiln step at removing moisture from the flux could be estimated. Figure 3.11 illustrates the technique on the TG curve for calcium silicate. Only the mass loss from room temperature to the high kiln temperature was considered as the kiln loss. The total loss would give the total moisture content of the component. The moisture content data from Table 3.1 and predicted moisture content removed by the high temperature kiln are given in Table 3.2. From this data it can be seen that nearly all of the moisture

Figure 3.11 Method of determining the expected moisture loss for the high temperature kiln using calcium silicate as an example. The red line represents the temperature of the kiln. Any loss up to this temperature can be expected to be removed by the kiln. The total weight removed is the total loss or total moisture content of the sample.

<table>
<thead>
<tr>
<th>Component</th>
<th>CaSiO₃</th>
<th>Li₂CO₃</th>
<th>MnO</th>
<th>CaF₂</th>
<th>MgO</th>
<th>TiO₂</th>
<th>CaSi₂</th>
<th>Al₂O₃</th>
<th>CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (wt%)</td>
<td>0.59</td>
<td>0.57</td>
<td>0.42</td>
<td>0.35</td>
<td>0.24</td>
<td>0.19</td>
<td>0.14</td>
<td>0.55</td>
<td>0.03</td>
</tr>
<tr>
<td>Moisture content removed (wt%)</td>
<td>0.26</td>
<td>0.56</td>
<td>0.41</td>
<td>0.32</td>
<td>0.21</td>
<td>0.17</td>
<td>0.14</td>
<td>0.45</td>
<td>0.03</td>
</tr>
</tbody>
</table>

from the components is removed by the kiln, with the exception of calcium silicate. This would mean that the moisture content of the flux can be expected to be near that of the components. In order to determine this, the moisture content of the flux was calculated from the rule of mixtures. By using the composition of the flux and the moisture content the components moisture content was calculated to be 0.35 weight percent. From the data previously presented the average flux moisture content was found to
be 0.76 weight percent. The gain from the initial products indicates that during production there was a gain of moisture.

To determine where in the production process the moisture pickup is, the production process itself was broken down into several steps. The findings from this breakdown are shown in Figure 3.12. A large pickup in moisture from the addition of the binder was observed, this increase was to be expected as a water based binder was used. The moisture added from the binder would then driven out during the kiln treatments. The results show another pickup in moisture content after the cooling steps. However if the error in the process is taken into account it may be that the difference falls within in the standard deviation of the results as the difference is rather small between the last three steps.

![Figure 3.12](image.png)

**Figure 3.12** Moisture content for steps of production of flux. Each step had a flux sample taken after each step. The samples were tested by DTA-STA for moisture content.

A welding consumables company conducted separate analysis using a Leco RC612 analyzer. These results are given in Table 3.3. From the comparison of the data with results reported earlier in the document it is seen that there are large differences in the data after the disc agglomerator. Since these are an analysis of the flux and not the components the differences could be contributed to carbonate decomposition. If the DTA-STA is not able to discern the carbonate decomposition in the flux a larger mass will be attributed to moisture loss. When the flux is in the form of a wet mix its high moisture content and moisture loss during the test were large enough hide any other losses. After the first kiln heat treatment the moisture loss is no longer enough to mask the carbonate loss and the carbonate decomposition contributes will affect the weight loss observed for the low temperature kiln step. With
some calcium carbonate already decomposed the mass loss in the last two steps will be similar. Additionally the fluidized bed cooler should not add any moisture to the flux given that humid air is not used in that step.

Table 3.3 – Moisture content results for differing methods. The External result refers to the RC612 analyzer and CSM result refers to DTA-STA.

<table>
<thead>
<tr>
<th></th>
<th>wt% water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>External Result</td>
</tr>
<tr>
<td>Disc agglomerator</td>
<td>8.64</td>
</tr>
<tr>
<td>LT Kiln discharge</td>
<td>0.24</td>
</tr>
<tr>
<td>Fluid bed cooler Inlet</td>
<td>0.024</td>
</tr>
<tr>
<td>Fluid bed cooler discharge</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Contrarily, the Leco RC612 analyzer is able to distinguish the carbonate loss from the moisture loss. As the sample is heated in a stream of gas, it uses two infrared detectors to determine the water and carbon dioxide contents in the gas stream. On the other hand, DTA-STA cannot do this without evolved gas analysis (EGA) using a mass spectrometer or Fourier transform infrared spectroscopy (FTIR).

To continue testing and accommodate for the analysis limitations of DTA-STA a second method, vacuum degassing, was used. If all moisture in the flux is assumed to be absorbed or adsorbed then it should be possible to drop the pressure low enough to pull it out as vapor without affecting the carbonates. Using this method any mass lost during testing can be attributed to moisture.

Testing was done in a vacuum furnace that could achieve a vacuum greater than 5x10^{-5} Torr. The tests occurred at room temperature to avoid any sublimation or melting of the flux components. Testing was done again using this process for samples collected from all stages of flux production. The results for all three types of testing are presented in Table 3.4. From a first glance it is noticed that the results of the vacuum degassing match those found by the consumables supplier better than the DTA-STA results, with the exception of the low temperature kiln discharge. The discrepancy was not resolved at the conclusion of this study. It may be that a hydrate formed in the low temperature kiln and the vacuum alone was not enough to remove water of crystallization.
Table 3.4 – Comparison of methods for moisture content. External result refers to RC612 analyzer, CSM result refers to DTA-STA. Vacuum refers to moisture content determined by vacuum degassing.

<table>
<thead>
<tr>
<th>Component</th>
<th>wt% water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>External Result</td>
</tr>
<tr>
<td>Disc agglomerator</td>
<td>8.64</td>
</tr>
<tr>
<td>LT Kiln discharge</td>
<td>0.24</td>
</tr>
<tr>
<td>HT Kiln discharge</td>
<td>0.024</td>
</tr>
<tr>
<td>Fluid bed cooler discharge</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Redetermining the flux moisture content as well using the vacuum degassing, the flux was found to have a moisture content of 0.028 weight percent which is significantly lower than the moisture content of 0.73 weight percent determined by DTA-STA. With this new moisture content for the flux it can be seen that that all of the moisture added during production is removed from the flux. A comparison of the moisture contents obtained by both methods is given in Table 3.5. moisture content as a flux is increased when the vacuum degassing was used. The higher moisture content of the flux is counterintuitive as it would be expected that the moisture content would decrease if the DTA-STA data is an overestimation with mass loss included that was not moisture. Comparing the individual moisture contents it can be seen that some components do have a drop in moisture content, while some have a rather large increase. Since it is unlikely that the components sublimed during vacuum degassing, the gain in moisture content is attributed to moisture pickup.

Table 3.5 – Moisture content of components using vacuum degassing. Results from the DTA-STA are included for comparison. Flux refers to the moisture content of the components as a flux using the law of mixtures and the flux composition.

<table>
<thead>
<tr>
<th>Component</th>
<th>MgO</th>
<th>MnO</th>
<th>CaF₂</th>
<th>CaSiO₃</th>
<th>CaSi₂</th>
<th>FeTiO₃</th>
<th>Al₂O₃</th>
<th>Li₂CO₃</th>
<th>CaCO₃</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTA-STA</td>
<td>0.24</td>
<td>0.42</td>
<td>0.35</td>
<td>0.59</td>
<td>0.14</td>
<td>0.19</td>
<td>0.55</td>
<td>0.57</td>
<td>0.03</td>
<td>0.35</td>
</tr>
<tr>
<td>Vacuum</td>
<td>0.03</td>
<td>0.22</td>
<td>0.74</td>
<td>1.62</td>
<td>1.57</td>
<td>0.76</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>0.50</td>
</tr>
</tbody>
</table>
From the analysis of the flux production it was noted that the addition of the silicate binder had the largest contribution of moisture. Silicates are used because of their ease of use and adaptability to all flux processes. However most of the common silicate binders are water based which adds moisture to the flux. So the identification of a new binder that can avoid adding the large amount of moisture is needed. There are binders that are not water based such as polymers or sol-gels[48], [49]. However they are not as adaptable to the process of agglomeration even though it is possible to achieve a lowering of the diffusible hydrogen content.

3.2 Wire and base Metal Evaluation

Below is presented the results of the wire and base metal characterization. Several total hydrogen measurements were carried for various conditions of the wire. The base metal was characterized in the as-received condition. It was assumed that there was no diffusible hydrogen present in the materials to simplify the analysis of the results.

3.2.1 Wire Hydrogen Content

The wire was first analyzed for hydrogen content in the as received condition. Table 3.6 shows the hydrogen content for the wires in the as-received condition. From these results it is only possible to perform a comparison between the wires themselves. Wire two was found to have a hydrogen content that is

<table>
<thead>
<tr>
<th>Sample Weight (g)</th>
<th>PPM Hydrogen</th>
<th>Average PPM Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.041</td>
<td>1.03</td>
<td>1.07</td>
</tr>
<tr>
<td>0.978</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>1.223</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Wire 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.736</td>
<td>2.84</td>
<td>2.71</td>
</tr>
<tr>
<td>0.915</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>0.765</td>
<td>2.77</td>
<td></td>
</tr>
<tr>
<td>Wire 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.875</td>
<td>1.01</td>
<td>1.28</td>
</tr>
<tr>
<td>0.768</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>0.624</td>
<td>1.48</td>
<td></td>
</tr>
</tbody>
</table>
double that of the other wires. It was originally thought that this large difference in the wires could be the result of an overabundance of lubricant on the surface of wire two. The excess lubrication was rationalized by the fact that two wires of the same diameter should not have a large difference between them for the same production process. The lubricant coating may vary from wire to wire as it is located on the surface; some may acquire more or less during production due to natural variations in machinery.

If the variation is due to the presence of lubricant then washing the wires should yield a closer result between wire two and wire three because of similar diameter. The results of washing the wire are given in Table 3.7. From these results it is seen that the lubricant is not responsible for the large

difference in hydrogen content between the wires. The amount removed was not consistent for all of the wires and the difference in hydrogen content between wires two and three could not be explained. The inconsistency after the lubricant is removed indicates that there is either a difference in the production of the two wires, or that there might be a large amount of residual hydrogen in the core wire used.

The unknown contribution was easily remedied with the removal of the coating. The hydrogen content for the bare base wires is given in Table 3.8. The data shows that the core wires had similar hydrogen content. To compare the contributions from each part of the wire the values are subtracted from the total and given in Table 3.9. Here it is seen that the lubricant is not consistent across the wires. Nor is the hydrogen content of the copper coating consistent. Since the lubricant and core wire could not

### Table 3.7 – Total hydrogen content for wires washed in acetone. This total would include contributions from the coating and base wire.

<table>
<thead>
<tr>
<th></th>
<th>Sample Weight (g)</th>
<th>PPM Hydrogen</th>
<th>Average PPM Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire 1</td>
<td>1.059</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.796</td>
<td>0.85</td>
<td>0.94</td>
</tr>
<tr>
<td>Wire 2</td>
<td>0.918</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>1.013</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.917</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>Wire 3</td>
<td>1.004</td>
<td>0.79</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>0.804</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.127</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>
account for the significant difference between the wires, the copper coating on the wires appears to be the be the source of the difference. Even between wires of the same diameter and the same production process there is a significant difference in the copper coating.

The only hydrogen content that is consistent is that of the base wire. From these values it is seen that the contribution from the coating and lubricant is about equal in Wire 3. But for the other wires the coating contributes more to the hydrogen content than the lubricant present. The process used to coat the wires in copper is electrolytic deposition. So it can easily be rationalized that there may be some form of hydrogen trapped in the coating, however the large difference between the wires is still unexpected.

Since the copper coating is the cause of the discrepancy, it is necessary to determine if it was a simple difference in the coating thickness or hydrogen trapped in the coating in some form. To determine the coating thickness four wire segments were cut from each wire. These segments were ground to a flat one end so the cross section of the wire would be placed in a mold and then mounted in epoxy with steel ball bearings. Each wire had its four wire segments in its own mount. The ball bearings were included to increase the surface area so that the mount would polish evenly and help with edge retention of the wire where the copper coating is located. The wires were then polished using steel polishing procedures with

<table>
<thead>
<tr>
<th>Wire</th>
<th>Sample Weight (g)</th>
<th>PPM Hydrogen</th>
<th>Average PPM Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.918</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>1.038</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.885</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.871</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>0.886</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.958</td>
<td>0.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.852</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.922</td>
<td>0.42</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>1.067</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.023</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.235</td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.8 – Total hydrogen content for base wire. This content represents only the hydrogen that is present in the base wire used for the welding wire consumable.
grit paper, diamond suspensions and a final polishing step with 0.05 micron alumina slurry. The wire cross sections were then analyzed on an Olympus PMG3 light optical microscope with a Paxcam digital camera. Figure 3.13 shows the copper coating on a segment of wire 2. To measure the coating thickness images were taken for each of the wire segments at the compass points. It is important that the cross section viewed be a perpendicular to the wire length so that the true thickness of the coating is measured.

Table 3.9 – Hydrogen contributions from each part of the wire. All values are in PPM hydrogen.

<table>
<thead>
<tr>
<th></th>
<th>Lubricant</th>
<th>Copper Coating</th>
<th>Base Wire</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire 1</td>
<td>0.12</td>
<td>0.48</td>
<td>0.46</td>
</tr>
<tr>
<td>Wire 2</td>
<td>0.71</td>
<td>1.54</td>
<td>0.46</td>
</tr>
<tr>
<td>Wire 3</td>
<td>0.43</td>
<td>0.41</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Figure 3.13 Copper coating of Wire 2. Light region is the steel wire and black is the mount, with the layer between consisting of the copper coating.

The images taken from the wire segments were then placed in an image processing program and nine measurements were taken from each image. The measurements were accomplished using line lengths that were calibrated to the micron marker in the images. These values were averaged from at least three wire segments for average coating thickness of the wire. Table 3.10 gives the values of the coating thickness for the wires.

From these values it is noted that the coating thickness on wire 2 is nearly twice that of wire 3. The difference in coating thickness would account for the wire 2 having double the hydrogen content of wire 3 if it is assumed that the wire coating has a constant hydrogen content.
Table 3.10 – Copper coating thickness values.

<table>
<thead>
<tr>
<th>Wire</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Thickness (μm)</td>
<td>1.56</td>
<td>1.35</td>
<td>0.79</td>
</tr>
</tbody>
</table>

However wire 1 had the thickest copper coating, yet it had a hydrogen content similar to that of wire 3. Since wire 1 is of a larger diameter a direct comparison of the wires may not be the best method. Instead comparing the coating area to the area of the core wire would give a ratio that can be compared among the wires. The values for the areas of the coatings and wires as well as the ratio of the areas are given in Table 3.11. From these values it is seen that wire 1 has a larger coating area than the other two wires.

Table 3.11 – Areas of the core wire and copper coatings of the wires. The ratio of the coating area and core wire area is also included so wires can be compared directly.

<table>
<thead>
<tr>
<th>Wire</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area of core wire (in²)</td>
<td>0.019</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>Coating area (in²)</td>
<td>3.02E-05</td>
<td>2.05E-05</td>
<td>1.18E-05</td>
</tr>
<tr>
<td>A_{coating}/A_{core}</td>
<td>1.57E-03</td>
<td>1.67E-03</td>
<td>9.65E-04</td>
</tr>
<tr>
<td>Hydrogen in Coating (PPM)</td>
<td>0.48</td>
<td>1.54</td>
<td>0.41</td>
</tr>
</tbody>
</table>

this finding is reasonable since it had a thicker coating and a larger diameter wire. However the ratio of coating to core wire is similar to that of wire 2. Wire 3 had the smallest ratio and the lowest hydrogen, which is expected if the coating hydrogen is consistent. Wire 1 had the largest coating, but wire 2 has a larger hydrogen content with a smaller coating. This indicates that the hydrogen content in the coating is not consistent. Comparing the coating areas to the core wire area, which has a similar hydrogen content, it is seen that wire 1 has a similar ratio to wire 2. This would infer that the hydrogen content would be similar, but since it isn’t it means that the coating has an inconsistent hydrogen content. This difference may occur from coating process differences for the wires.

Since hydrogen mitigation is the overall goal of the project, baking of the wires was conducted. The baking program was outlined in Section 2.2.1. Since wire 2 had the most hydrogen present it was chosen for the baking experiments. The results of the baking are shown in Figure 3.14. All but one heat treatment lowered the hydrogen content of the wire. Baking at 650°C for one hour raised the hydrogen content of the wire. This increase in the hydrogen content is attributed to the heavy oxidation of the wire.
The heat treatments were carried out in an air atmosphere and air cooled. So the oxidation was expected to occur at higher temperatures in an air atmosphere and air cooled. So the oxidation was expected to occur at higher temperatures.

Figure 3.14 Results of wire baking in atmosphere for Wire2. The values are for total hydrogen. The hydrogen contents for Wire 2 in the as received condition and the base wire are included for reference.

The wires that were baked at 450°C were also oxidized, but the extent of the oxidation was not as severe as that of the 650°C bake. The oxidation difference was noted by the lowering of the hydrogen content of the wires. The amount of oxidation does seem to play a role in the hydrogen content. Between the wires baked at 450°C, the one hour bake had a lower hydrogen content than the two hour bake. The two hour bake would have a longer time to form the oxide or any other reaction products that would again capture what was lost initially. The role of the oxide is confirmed with the 200°C baked wire. It had no visible oxide on the surface of the wire. The copper coating did undergo a color change, going from the reflective copper color to a duller red/copper color. The color change was the only visible difference that occurred during the baking. Since no oxidation occurred, and likely little diffusion occurred as well, the hydrogen content of the wire was reduced the most. The lowering of the hydrogen
content would be due to a temperature that is high enough to drive hydrogen from the coating, yet low enough to avoid any unwanted reactions that would start to recapture moisture.

In an attempt to see how low of a hydrogen content could be achieved and to prove that oxidation was the cause of the hydrogen content raise, one last heat treatment was performed. This time the wire was baked in a vacuum furnace at 650°C for one hour. The two heat treatments would provide a basis of comparison to determine the cause of hydrogen pickup. Table 3.12 gives the results of the vacuum baking as well as useful comparison points for hydrogen content of the wire. From these results the most notable point is that the hydrogen content was lowered to below that of the base wire. The lowering of the hydrogen content to below

Table 3.12 – Total hydrogen content for Wire 2 after baking in vacuum furnace with previous baking results for reference.

<table>
<thead>
<tr>
<th>Condition</th>
<th>450°C 1hr</th>
<th>450°C 2hr</th>
<th>650°C 1hr</th>
<th>200°C 1hr</th>
<th>As received</th>
<th>Base wire</th>
<th>650°C 1hr Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPM Hydrogen</td>
<td>1.58</td>
<td>1.99</td>
<td>5.82</td>
<td>0.67</td>
<td>2.71</td>
<td>0.46</td>
<td>0.23</td>
</tr>
</tbody>
</table>

the base wire means that hydrogen is driven out of the coating and that trapped hydrogen was being released and removed from the core wire. There was no visible oxidation at the surface of the wire baked in the vacuum furnace, as would be expected. Since the vacuum baked wire had no oxidation and a tremendous decrease in hydrogen when compared with the air baked wire it can be concluded that oxidation plays a strong role in the hydrogen content during baking. The increased hydrogen content is mainly due to the presence of cupric oxide that will pick up moisture from the atmosphere

The extent of the contribution of the wire hydrogen to the total hydrogen was also unknown. The effect can, however, be estimated as the PPM values for hydrogen are 10 percent larger than ml/100g, which is the unit of measure for diffusible hydrogen [51]. For example, the hydrogen content of wire 2 being 2.71 PPM will yield 2.44 ml/100g of diffusible hydrogen, if all hydrogen is assumed to transfer to the weld pool.

These numbers show that of a system that is capable of achieving 4 ml/100g of diffusible hydrogen using a wire with a hydrogen content similar to that of wire 2 of this study, half of the diffusible hydrogen is contributed from the wire. However, not all of the hydrogen will be converted to diffusible hydrogen. Additionally there is resistive heating that occurs in the wire [52] that would drive the hydrogen out of the wire and not transfer into the weld pool. There is also hydrogen that will become trapped at sites and will not contribute to the diffusible hydrogen content. So the total contribution of the
wire will be reduced from the as-received hydrogen content. However reduction of any hydrogen will be helpful to the final lowering of weld hydrogen.

How this information can be applied to the industry is also of importance. When the wire comes in a 50 lb spool it is possible to do a batch heat treatment of the wire. However when the wire comes in a 500 lb drum it becomes more difficult to do batch heat treatments. This is especially true if the welding occurs in a shipyard where it is humid and the hydrogen may be picked up again. It is possible to apply this information directly to the welding setup with minimal changes. A small quartz heater or induction coil can be introduced to the wire feed to the welder. Since only a low temperature needs to be achieved the heating element can be located close to the welder. Here it can heat the welding wire prior to its entry to the welder and remove hydrogen without damaging the equipment or requiring a large heat treatment facility. Additionally the proximity to the welder will help to eliminate the time the wire has to recapture hydrogen.

3.2.2 Base Metal Hydrogen Content

Since the base metal may also be a source of hydrogen it was also analyzed. The results of testing are seen in Table 3.13. The base metal was found to have a total hydrogen content near one PPM. Any hydrogen present in the base metal should be in the form of residual or trapped hydrogen. Any surface contaminants or hydrides that may be present in the rust on steel should be removed during weld prep. The hydrogen content of the base metal was found to be lower than that of wires. Therefore it can be assumed that it will have a contribution approximately equal to that of the wire. Unlike in the wire where it is relatively easy to remove the hydrogen, the base metal presents several problems. For applications involving SAW the base metal is generally large plates, which makes heat treating them for hydrogen removal rather troublesome. Vacuum heat treatment is impractical. A pre-heat may be used for

<table>
<thead>
<tr>
<th>Weight(g)</th>
<th>PPM Hydrogen</th>
<th>Average PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.853</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>0.897</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>0.916</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>0.582</td>
<td>0.7</td>
<td>0.98</td>
</tr>
<tr>
<td>0.735</td>
<td>1.86</td>
<td></td>
</tr>
</tbody>
</table>
welding, but it may not be at a high enough temperature or long enough to release hydrogen. Therefore it is unlikely that the base metal hydrogen can be readily mitigated without changes to mill processing of the steel.

3.3 Fluoride Refinement and Selection

Since the number of fluorides is too large, it was necessary to use selection methods to refine the number of fluorides that would be tested. Even though this work tries to be comprehensive, there was not data available for all fluorides to be evaluated. Additionally the availability of fluorides also determined if a fluoride would be investigated. The data presented here is for the fluorides that had data available and were available for research.

3.3.1 Thermodynamic Calculations

The first reaction investigated through thermodynamic calculations was the thermal decomposition of the fluorides into fluorine and its components. Calculations were carried out for fluorides where thermodynamic values were available for Equation 2.3. The results of the thermodynamic calculations for the thermal decomposition of the fluoride are given in Figure 3.15. No complex fluorides were included in the calculations not knowing the actual decomposition steps. The red line on the graph is representative of the high temperature kiln temperature of 705°C. Comparing the predicted temperatures against the kiln temperature it is seen that none of the fluorides with values that could be obtained will decompose during production of the flux. While the decomposition temperatures seem high for conventional heating applications, such as ovens or furnaces, the temperatures achieved in a welding arc will be sufficient to achieve thermal decomposition of the fluorides [53]. Given that none of the fluorides can be removed based on the basis of a low thermal decomposition, all of the fluorides can be moved to the second calculation.
The second reaction considered was the reaction between the fluoride and water present in the flux to produce HF and an oxide. While every fluoride passed the initial screening there were several oxides that did not have thermodynamic data available and were left out of the second set of calculations. However complex fluorides were included, as there was data available for their oxides or a complex oxide that would form, such as KBO$_2$ which would form from KBF$_4$. The predicted temperatures are presented in Figure 3.16. On the figure the green line represents the high temperature kiln and the red line is a reference to the CaF$_2$ reaction temperature. As CaF$_2$ is currently the fluoride of choice in the flux it is useful to compare the predicted reaction temperature of other fluorides to it. The reaction would occur due to the heating of the flux immediately ahead of the arc and weld pool. While Figure 3.16 presents all of the reaction temperatures, it is skewed by the highest reaction temperatures. To better compare the higher temperature reactions have been removed and the modified set of temperatures is given in Figure 3.17. Unlike the decomposition temperature, there are fluorides that have a predicted reaction temperature below that of the high temperature kiln. Therefore these fluorides can be removed from the pool of possible fluorides for use in the flux, as the formation of HF is to be avoided during production. The remaining fluorides would all be viable fluorides for use in the flux.
Figure 3.16  Calculated reaction temperature for fluoride with water. The green line represents the high temperature kiln. The red line is a reference to the CaF$_2$ reaction temperature.

Figure 3.17  Calculated reaction temperatures for fluoride with water, with high reaction temperature fluorides removed from set. The green line represents the high temperature kiln. The red line represents the CaF$_2$ reaction temperature for reference.
3.3.2 Fluoride Decomposition in an Arc

Based on the thermodynamic calculations it was possible to remove some fluorides. However the pool of possible fluorides, twenty three, is still very large. Therefore further refinement of the list was necessary. To accomplish further reduction the behavior of the fluorides in a welding arc was tested. Due to the still large number of possible fluorides, those that were readily available or recommended by industry were tested. Eleven fluorides remain and they are: CaF$_2$, NaF, SrF$_2$, K$_3$AlF$_6$, K$_2$TiF$_6$, MgF$_2$, KBF$_4$, Na$_2$TiF$_6$, K$_2$SiF$_6$, Na$_2$SiF$_6$, KF. CaF$_2$ was included as a reference for comparison. KBF$_4$ was also included in the group even though it has a reaction temperature lower than the high temperature kiln as it had high performance in experiments [34].

The criterion for the decomposition in the arc experiments was weight reduction, assuming that all mass lost was due to fluorine loss. The reductions in weight as percentages are shown in Figure 3.18. From this graph it is seen that every fluoride had a better decomposition behavior than CaF$_2$. The two fluorides with the best performance were KF and Na$_2$SiF$_6$ as they had the highest mass loss. The worst fluorides were NaF, SrF$_2$, and K$_3$AlF$_6$. CaF$_2$ was also one of the worst performing fluorides, but this was expected due to its limited dissociation.

By assuming that the binder behaves similarly with all fluorides, it can be removed from this series of tests. With this consideration, the data that was collected should be related to the decomposition temperatures that were calculated previously. Any mass lost is essentially assumed to be the fluoride decomposing and its subsequent removal. The comparison of the calculated decomposition temperature and the actual decomposition in the arc is shown in Figure 3.19. Seen from the comparison is that there is a trend where mass loss is increased with a decreasing decomposition temperature. However the trend is not as clear as would be expected if it was assumed that all loss of fluorine was due to decomposition. Therefore it is safe to say that there is some mass loss that is not attributed to the fluorine. The extra mass loss could be due to the vaporization of the other elements present in the fluoride that are also removed during the test.

When the decomposition temperatures are compared to a theoretical arc temperature the behavior is explained. Typical arc temperature would exceed by much any of the predicted decomposition temperatures. This large overshoot in temperature means that the weld system is no longer in a regime where the decomposition temperature may determine what happens to the fluoride. So the behavior may not occur as would be expected by the prediction of the temperature alone in the fluoride. Taking all these factors into consideration, the complex fluorides had the best decomposition behavior of the fluorides tested as was seen with their high reductions in weight.
Figure 3.18  Reduciton in weight of fluorides after exposure to a welding arc expressed as a percentage.

Figure 3.19  Reduction in weight of fluoride from exposure to a welding arc compared to calculated decomposition temperature. Note the broken scale for decomposition temperature.
3.3.3 Fluoride Decomposition in a Simple Flux

Since the decomposition of the fluorides could not truly predict the behavior in a flux in terms of fluorine loss further testing was done. This time the fluorides were incorporated into a simple flux. The fluorides tested in this manner were: CaF$_2$, SrF$_2$, KBF$_4$, K$_3$AlF$_6$, KF, Na$_2$TiF$_6$, and K$_2$SiF$_6$. NaF and MgF$_2$ were removed due to the poor decomposition behavior from the previous testing. SrF$_2$ was kept as it had the best behavior of the lowest decomposing fluorides, and it was reasoned that at least one noncomplex fluoride should remain. Na$_2$SiF$_6$ was removed as it was discovered that this fluoride would produce harmful products.

Once the fluoride containing fluxes were exposed to an arc analysis of the remaining flux was done using XRD. The resulting scans are given in the following figures: Figure 3.20 - Figure 3.27. The arrows indicate the characteristic peak for the fluoride in both the before and after scans. The largest peak present in every scan belonged to MgO. In the reacted scans there were varying degrees of the presence of an “amorphous hump”, which is expected as the melting of oxides will form a glass with no distinct diffraction peaks. KF had the best amorphous “hump” occurrence seen in Figure 3.27 B.

To process the scans to quantify the diffraction peaks the data was modified for use with the XRD software. First the CuK$_{α2}$ peaks were stripped from the scans. Then the background was stripped from the scans. The stripping of the background removes the curvature from the front half of the scans and makes the scan profile flat with peaks. Initially identification of the fluoride peaks was attempted using peak matching software. However, due to the complexity of the scan results the software was found to be unreliable in peak matching. It was possible to match the before scans to peaks for the fluorides, but not for the reacted scans. So instead the fluoride peaks were identified manually using the location of the characteristic peak for each fluoride.

The identification of the fluoride peak was easily done for all fluorides in the before scans except for KF. This is surmised to be due to a reaction that happened during the making of the flux. The flux containing KF was not easily formed as it made a very fluid compound after sitting rather than a formable paste like the other fluoride-containing fluxes. Therefore it is assumed that the fluoride reacted and very little of the fluoride actually remained in the flux. A small peak was identified that matched the characteristic peak. For the reacted scan of KF the peak location for the fluoride falls in the “amorphous hump”. The background at the region where the KF peak would have been located is higher than that of the peak in the before scan. Therefore the peak intensity for KF in the reacted is assumed to be zero.
Figure 3.20  XRD scans of simple flux containing CaF$_2$.  A.) Scan of flux before exposure to arc.  B.) Scan of flux after exposure to arc.  Arrows indicate location of characteristic peak of the fluoride.
Figure 3.21  XRD scans of simple flux containing K₂TiF₆.  A.) Scan of flux before exposure to arc.  B.) Scan of flux after exposure to arc.  Arrows indicate location of characteristic peak of the fluoride.
Figure 3.22  XRD scans of simple flux containing SrF$_2$. A.) Scan of flux before exposure to arc. B.) Scan of flux after exposure to arc. Arrows indicate location of characteristic peak of the fluoride.
Figure 3.23 XRD scans of simple flux containing $K_3AlF_6$. A.) Scan of flux before exposure to arc. B.) Scan of flux after exposure to arc. Arrows indicate location of characteristic peak of the fluoride.
Figure 3.24 XRD scans of simple flux containing $K_2SiF_6$. A.) Scan of flux before exposure to arc.  B.) Scan of flux after exposure to arc. Arrows indicate location of characteristic peak of the fluoride.
Figure 3.25  XRD scans of simple flux containing Na$_2$SiF$_6$.  A.) Scan of flux before exposure to arc.  B.) Scan of flux after exposure to arc.  Arrows indicate location of characteristic peak of the fluoride.
Figure 3.26 XRD scans of simple flux containing KBF₄. A.) Scan of flux before exposure to arc. B.) Scan of flux after exposure to arc. Arrows indicate location of characteristic peak of the fluoride.
Figure 3.27  XRD scans of simple flux containing KF.  A.) Scan of flux before exposure to arc.  B.) Scan of flux after exposure to arc.  Arrows indicate location of characteristic peak of the fluoride.
For the fluxes containing the other fluorides, peaks were found in the reacted scans. The signal noise in the scans made it difficult to locate the peaks, but a peak for each fluoride was located. After this analysis a peak intensity was identified for each fluoride from its characteristic peak in the before and reacted state. Due to the vast difference between the fluorides x-ray behaviour a direct comparison of the peak intensities cannot be done. Therefore a normalization of the peaks needs to be done. Since MgO had the most intense peak of all the compounds present in every XRD scan, each of the fluoride peaks was normalized to the MgO characteristic peak assuming that MgO behaved similarly in every test. To normalize the peaks Equation 3.2 was used where I is the intensity of the peak of interest. \( I_{\text{max}} \) is the most intense peak of the scan, and \( I_n \) is the normalized peak intensity [54]. The difference between the normalized peaks of a fluoride is then assumed to be the decomposition of the fluoride in the arc.

\[
I_n = \frac{I}{I_{\text{max}}} \tag{3.2}
\]

By comparing the reductions in the normalized peaks it is possible to compare the fluorides for their behavior in a welding arc. Figure 3.28 gives the normalized peak intensities for the fluorides. It shows both the before and reacted intensities as well as the reduction between the peaks. The fluoride that exhibited the largest reduction in fluoride intensity was SrF\(_2\). Since KF had an assumed reacted peak intensity of zero it was excluded from comparison. An additional unexpected result was that KBF\(_4\) had the lowest peak reduction of all the fluorides tested. This fluoride was expected to have a much better peak reduction due to previous work in FCAW.

From this data it was possible to make recommendations for the fluorides to be used in experimental fluxes. SrF\(_2\), K\(_3\)AlF\(_6\), K\(_2\)TiF\(_6\), K\(_2\)SiF\(_6\) were recommended for the experimental fluxes. CaF\(_2\), with the low peak reduction, was retained as the control. LiF replaced K\(_3\)AlF\(_6\) because it was not readily available for the manufacture of the experimental flux LiF at their request.

Even though the x-ray analysis provided a good basis for the selection of fluoride ingredients to incorporate in the experimental fluxes, it is important to note that the analysis of the fluorides using XRD was semi-quantitative. To further the work done here it would be beneficial to use a method such as Rietveld analysis for XRD that is more quantitative. Alternatively, the amount of cation in the flux can be determined instead of the fluorine.
3.4 Diffusible Hydrogen Content of Experimental Fluxes

The experimental fluxes were designed to reduce hydrogen. The selection of the fluorides was presented in Section 3.3. Their ability of reducing hydrogen was tested according to AWS A4.3. The hydrogen collected was measured from the eudimeters in ml utilizing Equation 2.6, and then normalized to 100g of weld metal deposited. The values for each weld test are given in Table 3.14. To better visualize the data given in Table 3.14 the values for diffusible hydrogen are given in Figure 3.29. Here it is seen that the control experimental flux is similar to that of the industrial produced flux. None of the fluoride-bearing fluxes were able to lower the diffusible hydrogen content below that of the unmodified flux. Additionally the fluorides that were chosen can be separated into two groups.

The first being the fluorides that did not lower the hydrogen content, but instead raised it significantly. This behavior was attributed to changing arc behavior. During welding it was noted that the fluxes containing LiF and K2TiF6
Table 3.14 – Diffusible hydrogen measurements for experimental fluxes. Control refers to EM12K flux produced through small batch process.

<table>
<thead>
<tr>
<th>Flux</th>
<th>V (ml)</th>
<th>H (mm)</th>
<th>Weight (g)</th>
<th>Weld Metal (g)</th>
<th>P (mmHg)</th>
<th>T (°C)</th>
<th>VH (ml STP)</th>
<th>Diffusible Hydrogen (ml/100g)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
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<td></td>
<td></td>
<td></td>
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<td>266</td>
<td>197.5</td>
<td>211.50</td>
<td>14.0</td>
<td>779.8</td>
<td>22.5</td>
<td>0.68</td>
<td>4.94</td>
</tr>
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<td></td>
<td>1.18</td>
<td>259</td>
<td>197.6</td>
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<td>779.8</td>
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<tr>
<td></td>
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<td>225</td>
<td>198.0</td>
<td>212.20</td>
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<td>0.99</td>
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<td>204.14</td>
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<td>211.29</td>
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<td>780.3</td>
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<td>195.6</td>
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<td>193</td>
<td>197.0</td>
<td>209.62</td>
<td>12.6</td>
<td>779.0</td>
<td>20.5</td>
<td>1.31</td>
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<td>780.0</td>
<td>20.9</td>
<td>0.74</td>
<td>5.60</td>
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</table>
did not outgas. Additionally they adhered to the weld and did not self release. They required more than one cleaning step per weld. The $K_2TiF_6$ weld showed signs of increased slag viscosity. Weld humping occurred with undercutting along the weld toe. LiF was less severe than $K_2TiF_6$, but the weld showed clear signs of increased flux viscosity.

The remaining fluoride-containing fluxes performed the same as the industrially produced flux. There was no problem with outgassing or adherence to the weld. However the diffusible hydrogen content of the weld was not reduced, but rather raised. The raise in diffusible hydrogen content is thought to be one of two possibilities. The first possibility being that not enough fluoride was added. Essentially the flux was modified enough that it changed how it interacted with hydrogen, but not enough of the reducing fluoride was added to make an impact. The second possibility is that the fluxes had too much starting moisture. The fluxes were used in the as-received condition from a commercial manufacturer. Therefore it is thought that the addition of the fluoride changed the hygroscopic nature of the flux and changed the starting moisture in the flux.
Here it should be noted that the welds were made on A36 steel plates and the welding wire was ER100-S1. As such the welds made would be overmatched for the base metal[55], [56]. If the weld was made on HY-80 plate the overmatch would be significantly lower. When the weld metal is overmatched with the base metal the flow of hydrogen will be from the heat affected zone towards the in the weld metal[14]. Thus the welds produced with the A36 steel may not be a true representation of where the hydrogen is in the weld and hence the diffusible hydrogen content.

To determine if the results are high due to moisture one last diffusible hydrogen test was conducted at CSM for this research. While this test was carried out to AWS specifications it did not meet the requirements for a valid test as one of the eudiometer tubes was broken prior to testing and only three weld samples were made instead of the required four. For this test the reference flux was used for welding, but it was baked before welding at 300°C for two hours immediately prior to welding. Samples were also taken of the flux before baking and after welding for moisture content determination by vacuum degassing. The industrially-produced flux already had this testing done and was found to have a moisture content of 0.028 weight percent. The moisture content for the fluxes before and after baking was found to be 0.030 and 0.009 weight percent respectively. The moisture content and diffusible hydrogen content for each flux is shown in Figure 3.30.

![Diffusible Hydrogen Content](image)

**Figure 3.30** Diffusible hydrogen content of EM12K fluxes with differing moisture contents. The lowest moisture content flux was baked and the remaining two fluxes were as received when used for testing. The trendline shows the great correlation achieved between moisture content in a flux and the diffusible hydrogen content.

By comparing the moisture content and the diffusible hydrogen level achieved it can be seen that there is a relationship between the two. The relationship between the two is not a new discovery as it has
been shown before that diffusible hydrogen content is related to the moisture present in a flux coating [24]. However this relationship can be extended to the remaining experimental fluxes and the some of the diffusible hydrogen content can be attributed to high moisture content in the fluxes.

The commercial manufacturer ran concurrent experiments with the fluxes after baking at 300°C for two hours. The tests were carried out according to AWS A4.3 and analysis was done using gas chromatography. The results that they achieved for the test are given in Table 3.15 as

Table 3.15 – Comparison of diffusible hydrogen results done at the Commercial manufacturer with flux baking and at CSM with as received flux. All values have units of ml/100g.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>SrF₂</th>
<th>K₂TiF₆</th>
<th>K₂SiF₆</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>External</td>
<td>3</td>
<td>3.4</td>
<td>3.8</td>
<td>5.6</td>
<td>4</td>
</tr>
<tr>
<td>CSM</td>
<td>5.23</td>
<td>5.8</td>
<td>12.5</td>
<td>7.72</td>
<td>10.33</td>
</tr>
</tbody>
</table>

well as the data from CSM for comparison. The diffusible hydrogen contents for the baked fluxes are lower than the results for the as-received fluxes. The lowering of diffusible hydrogen by baking is expected as the baking will remove any excess moisture that was picked up during shipping and storage during testing. The flux with K₂TiF₆ showed better performance, and the flux with K₂SiF₆ had the worst performance. The SrF₂ addition still had the best performance of the fluorides chosen. However none of the fluorides were able to reduce the diffusible hydrogen content of the welds below the control flux. From these experiments it can be concluded that none of the fluorides used in the experimental fluxes are effective at eliminating diffusible hydrogen from a weld at an addition of one weight percent. Additionally it is seen that even small additions to the flux may change the behavior and that further changes beyond the addition of a fluoride may be needed to optimize the flux[23].
CHAPTER 4: CONCLUSIONS

The effect of moisture content of EM12K flux on diffusible hydrogen content was determined. This research has performed an in depth characterization of the SAW system regarding moisture pickup. It has also characterized a number of fluorides for diffusible hydrogen reduction regarding moisture pickup and provided the starting work for further development of this field. From this investigation the results can be summarized in the following conclusions:

1. DTA-STA may be used for determining the moisture content of flux ingredients at CSM if coupled with EGA and platinum crucibles.
2. Vacuum degassing was introduced as a viable way of determining moisture content for welding fluxes.
3. The kiln drying process for agglomerated fluxes substantially removes the moisture that is added from the binder.
4. In a copper-coated welding wire, the copper coating is the largest source of hydrogen for the wire. The second largest source of hydrogen is lubricant left on the surface of the wire. Both of these sources are not a constant value between wires of same and varying diameters.
5. Baking at 200°C in atmosphere is sufficient to reduce the total hydrogen content of a copper-coated welding wire to near that of the base wire used. Vacuum baking at 650°C reduces the total hydrogen content of the wire to below that of the base wire used.
6. Fluoride decomposition temperature is not the determining factor for the effectiveness of a fluoride in a flux.
7. Normalized XRD peak reduction of a fluoride in a simple flux system predicts fluoride effectiveness better than decomposition temperature.
8. At a one weight percent addition the following fluorides are effective at reducing the diffusible hydrogen content of a weld below 4 ml/100g when added to EM12K flux: SrF₂, K₂TiF₆, and LiF.
CHAPTER 5: FUTURE WORK

Over the course of this research there were discoveries made that were out of the scope of this project. Additionally the time constraints of any project further limit what is feasible to be worked on or researched. The objective of this section is to identify the areas of research that can be further studied.

5.1 Flux Characterization

From the characterization of the flux ingredients and manufacturing process it was seen that the binder was the largest contributor of moisture to the flux. Silicate binders that are typically used are water based. It was alluded to in the results of the characterization that an alternate binder should be identified. The identification of a binder that is suitable for use in agglomerated fluxes that does not add significant amounts of moisture during production is still imperative, and may lead to ultra low hydrogen content welding fluxes.

The other note that can be made from the flux characterization results is that there is still moisture present in the flux after the high temperature kiln. If there is a way that this moisture can be removed then it will lower the diffusible hydrogen content that can be during flux manufacturing. Therefore a way to further reduce the moisture content of the flux after the high temperature kiln needs to be identified.

5.2 Wire Characterization

It was proven that there is an amount of hydrogen in the welding wire that can be removed. However it was not tested if there was any effect on the diffusible hydrogen content of the weld from the hydrogen present in the wire. Due to the resistive heating of the wire the actual amount of hydrogen that is transferred from the wire to the weld pool is unknown. By utilizing lengths of wire that have been baked in various conditions it would be possible to determine the actual effect the wire has on the diffusible hydrogen content of the weld.

5.3 Fluoride Characterization

From the results shown in this research it was clearly shown that data from FCAW is not directly applicable to SAW. The systems have distinct differences that prevent any correlation from being obtained as well as different flux systems. However the work done with the fluorides was basic enough that it is possible to bridge the welding processes. The simple flux that was used for testing of the fluorides may have been mixed just right to correlate data between sets of experiments. When the calculated peak reductions for the fluoride XRD tests are compared to the diffusible hydrogen results from Pokhodnya [33] a trend emerges. Figure 5.1 shows this trend with the four fluorides from both sets of tests. It can be seen that a decrease in diffusible hydrogen is correlated to an increase in peak reduction.
of the fluoride seen from XRD results. With this trend it may be possible to predict the effectiveness of a fluoride for use in reducing diffusible hydrogen. Therefore a wider range of fluorides should be evaluated that matches both sets of experiments to further investigate this correlation.

![Graph showing correlation between peak reductions and diffusible hydrogen content](image)

Figure 5.1 Diffusible hydrogen content attained from Pokhdyna [33] plotted against peak reductions obtained from XRD scans presented in this research.

Additionally during the XRD analysis of the reacted fluorides a possible match chosen by the XRD software was CaF₂. However, with the exception of the flux with specific CaF₂ addition, no other flux contained CaF₂ before being exposed to the arc. The presence of these peaks means that CaF₂ was created at some point during or after exposure to the arc. While the presence of the new fluoride was noted it was not discussed as the focus of the research was not solely on flux interactions. Additionally the work done with XRD was not done with the intent of quantifying the presence of CaF₂. Specific scans for CaF₂ would need to be run.

5.4 Diffusible hydrogen

To expand on this research several sets of experiments can be added. The set of fluorides used for the experimental fluxes could be expanded. The more data that can be added to this set will only better the understanding of the interactions that control the effectiveness of a fluoride.

In this research he fluorides were added to the flux at constant addition amount. The addition of the fluoride can be varied to see at what effect the weight percent of fluoride has on diffusible hydrogen.
The fluxes used were produced through traditional methods, i.e. with the fluoride addition being added into the dry mix ingredients. Using this method the fluorides had to be able to withstand and remain stable through the kiln heating of the flux production. However it may be possible to add the fluorides after the kiln treatments through a spray or other application technique. This procedure would open up the selection of possible fluorides to include any that had a predicted reaction temperature with water below that of the high temperature kiln. It would also open the possibility of using organic fluorides or polymers that would combust in the kilns. Additionally adding the fluoride after the flux is formed would limit its interactions with the flux in the production process. More fluoride would remain intact for removal of hydrogen during welding.

For future work done with these experimental fluxes it is important to know their behavior when scaling up the manufacturing process. This would include multi-pass welds and different polarities used during welding. Interpass behavior such as detachability and slag interactions with the weld become important. This way the entire performance of the system should be evaluated. Additionally when the process is scaled up the effect of fluoride on the health and welfare of the welders need to be studied.
REFERENCES


