# NIOBIUM REACTION KINETICS: AN INVESTIGATION INTO THE REACTIONS BETWEEN BUFFERED CHEMICAL POLISH AND NIOBIUM AND THE IMPACT ON SRF CAVITY ETCHING*
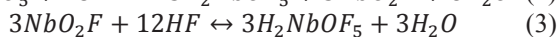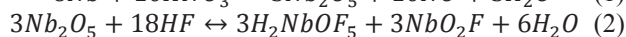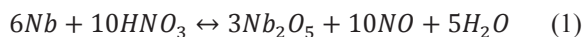
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## Abstract

In the SRF community, there is no definitive agreement on the precise reaction mechanism in the etching of niobium cavities by buffered chemical polish (BCP) mixtures. As a consequence, it is difficult to predict the heat produced during cavity etching. To gain a better understanding of the reaction kinetics of niobium and BCP, calorimetry experiments were performed to establish an experimental heat of reaction, and research was performed to determine a reasonable reaction scheme to allow for calculation of the theoretical heat of reaction. The results of the calorimetry experiments were in excellent agreement with one another and with the theoretical value. These results will allow for more accurate estimation of etch removal amounts on cavities without the need to perform time-intensive etch rate tests. Applying the experimental data to pre and post cavity etch ultrasonic thickness measurements has shown a significant improvement in the predictability of etch removal amounts in Facility for Rare Isotope Beams (FRIB) half-wave and quarter-wave resonators, and will allow for more reliable heat removal and prevention of Q-disease during other cavity etching procedures.

## INTRODUCTION

The standard BCP mixture used for etching superconducting RF cavities at FRIB is a 1:1:2 mixture of concentrated hydrofluoric (49% w/w), nitric (70% w/w), and phosphoric (85% w/w) acids. When this acid mixture contacts niobium metal, nitric acid oxidizes the surface layer of the metal, forming a niobium oxide film. The hydrofluoric acid then reacts with this niobium oxide layer to form hydrated niobic acid, which is solvated in the acid mixture. While this general reaction mechanism is well understood, there are many minor variations in literature regarding the intermediate species that are formed during the reaction. Due to these variations, the theoretical determinations of the heat produced during this reaction are unreliable. By combining experimentally supported reaction schemes [1, 2] into a unified mechanism, the reaction sequence for this experiment was defined as such:

$$6Nb + 10HNO_3 \leftrightarrow 3Nb_2O_5 + 10NO + 5H_2O \quad (1)$$
$$3Nb_2O_5 + 18HF \leftrightarrow 3H_2NbOF_5 + 3NbO_2F + 6H_2O \quad (2)$$
$$3NbO_2F + 12HF \leftrightarrow 3H_2NbOF_5 + 3H_2O \quad (3)$$

Combining the standard enthalpies of formation of these components [3] allowed a theoretical heat of reaction to be determined for comparison with the experimentally derived heat of reaction.

## HEAT CAPACITY EXPERIMENTAL

While the determination of the theoretical heat of reaction was relatively simple, it was impossible to determine the experimental heat of reaction without first knowing the specific heat capacity of BCP. Attempting to calculate the specific heat capacity of the mixture provided dissimilar results, depending on whether mass fraction or mole fraction was used as a basis (see Table 1).

Table 1: Theoretical Specific Heat Capacity of BCP

| Specie | Component Specific Heat (J/g/K) [3] | Mass Fraction | Mole Fraction |
|---|---|---|---|
| HF | 2.66 | 0.095 | 0.179 |
| $HNO_3$ | 1.74 | 0.166 | 0.100 |
| $H_3PO_4$ | 1.48 | 0.484 | 0.186 |
| $H_2O$ | 4.19 | 0.255 | 0.535 |
| Specific Heat of Mixture (J/g/K) | | 2.33 | 3.16 |

In order to determine which of the calculated values was most accurate, a heat transfer experiment was performed. A sample of the corrosion resistant alloy Hastelloy C-276, whose physical and thermal properties are well documented [4], was soaked in boiling ultrapure water (UPW) in order to heat it to precisely 100℃. The Hastelloy sample was quickly removed from the water and submerged in a small volume of BCP. The temperature change in the liquid was monitored with a thermocouple probe. This allowed the specific heat of the BCP to be determined with the following equation, where the subscript 'H' refers to the sample of Hastelloy:

$$c_{p,BCP} = \frac{m_H c_{p,H}(T_{H,i} - T_{H,f})}{m_{BCP}(T_{BCP,i} - T_{BCP,f})} \quad (4)$$

The average of the experimentally determined specific heat capacities of the BCP was 2.42 J/g/K. Since there is less than 4% error between the experimental value and the mass fraction basis theoretical value (as opposed to 30% error for the mole fraction basis), the mass fraction basis specific heat capacity was used for subsequent calculations.

## HEAT OF REACTION EXPERIMENTAL

The method of combining the standard enthalpies of formation of the reaction components is known as Hess's Law (see Eq. 5).

$$\Delta H^0_{reaction} = \sum \Delta H^0_{f,products} - \sum \Delta H^0_{f,reactants} \quad (5)$$

Applying Eq. 5 to the reactions detailed in Eq. 1-3, the theoretical heat of reaction is -678.9 kJ/mol niobium reacted [3, 5]. In order to confirm this value, calorimetry experiments were performed.

The experimental equipment was composed of a 400 mL polytetrafluoroethylene (PTFE) beaker, a PTFE coated magnetic stir bar, a PTFE coated thermocouple probe with a controller, a sample of virgin BCP with a mass of ~150 g, and approximately 100 small high-RRR niobium pellets (see Fig. 1).



Figure 1: Niobium pellets used during heat of reaction experiments.

The masses of the niobium pellets and the BCP sample were recorded with an analytical balance. The acid was poured into the beaker and stirred with the stir bar until the acid reached an equilibrium temperature. As soon as the acid temperature was constant, the niobium pellets were poured into the BCP mixture to begin the reaction, and the beaker was covered with a watch glass (see Fig. 2).



Figure 2: Orange nitric oxide vapors being formed during the reaction between BCP and niobium.

The temperature of the reaction mixture was recorded at 30 second intervals for five minutes, at which point the acid was dumped from the beaker to stop the reaction. The pellets were thoroughly rinsed with UPW to remove any residual acid, and were cleaned with electronic grade methanol to speed the drying process. Upon thorough drying, the mass of the pellets was recorded once more. Five experimental trials were performed in all.

To determine the heats of reaction from the experimental data, the change in mass of the niobium pellets was used to find the number of moles of niobium consumed in the reaction. Since the specific heat capacities of the BCP and niobium were also known, as was the change in temperature of the system, the heat evolved in the reaction was easily determined (see Fig. 3).
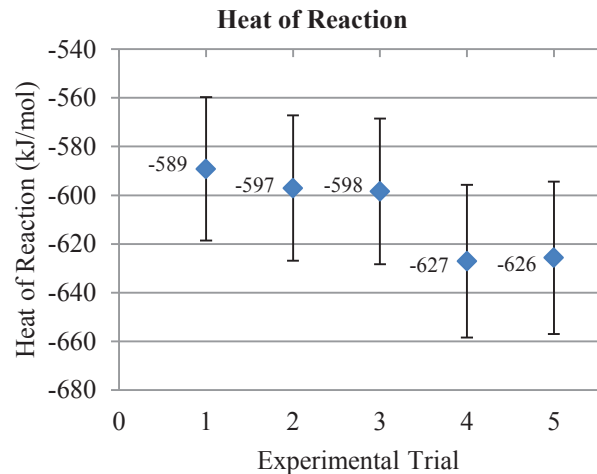


Figure 3: Heat of reaction experimental results (error bars represent ±5% of mean).

The average experimentally determined heat of reaction was -607 kJ/mol, with a standard deviation of 17.6 kJ/mol. This corresponded to a 10.5% difference between the experimentally determined and theoretical values of the heat of reaction.

## DISCUSSION

Although there was a slight difference between the theoretical and experimental heats of reaction, the results were very consistent. The reaction vessel used for this experiment was not insulated due to the difficulty of finding chemically compatible materials to use with BCP. If the radiative heat losses are neglected, and the reaction vessel is assumed to be perfectly stirred, the heat flow and total heat losses from the reaction mixture to the surroundings can be estimated with the following equations:

$$\dot{q}(t) = \frac{2\pi k_{PTFE}[T_i(t)-T_o]L}{\ln\frac{r_o}{r_i}} + \frac{\pi k_{PTFE}r_i^2[T_i(t)-T_o]}{B} \quad (6)$$

$$Q_{loss} = \int_0^t \dot{q}(t)dt \quad (7)$$
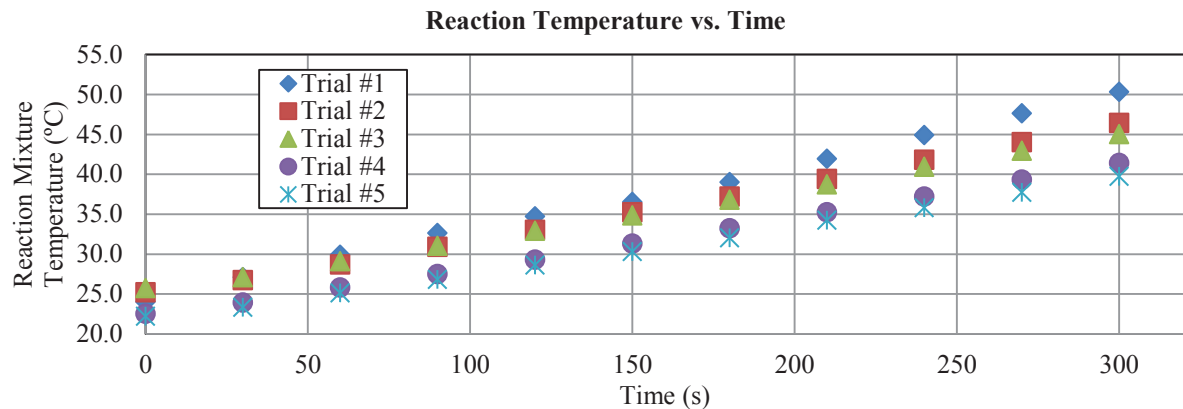
**Reaction Temperature vs. Time**



Figure 4: Experimental Time-Temperature Data.

The term $T_i(t)$ in Eq. 6 is the instantaneous temperature of the reaction mixture defined by the time-temperature function derived from the experimental data (see Fig. 4). For these experimental trials, the estimated heat losses were approximately 10% of the total heat released in the reaction. If these losses are taken into account, the average experimental heat of reaction is within 1% of the theoretical value.

The confirmation of this heat of reaction is significant because while etching SRF cavities, it is important to know how much heat needs to be removed from the cavity to prevent the cavity surface from becoming excessively heated. If surface temperatures are not monitored closely, hydrogen can begin to adsorb into the niobium, ultimately leading to decreased performance during cavity testing (Q-disease). The FRIB half-wave and quarter-wave cavities have helium vessels that can be used as heat exchangers during etching. Knowing the heat of reaction allows the required flow rate of cooling water through these helium vessels to be determined easily.

Similarly, knowing the heat of reaction allows the etch rate and total removal amounts to be determined and monitored in real-time simply by knowing the internal surface area of the cavity and the inlet and outlet temperatures and flowrates of the acid and cooling water flowing through the cavity. This eliminates the need for time-consuming etch rate tests and ultrasonic thickness measurements to determine the surface material removal during cavity processing, because a simple energy balance calculation is all that is required. Hundreds of cavities will be processed over the course of the FRIB project, so this has the potential to improve the repeatability of etching procedures performed both by FRIB and contracted vendors. Using the heat of reaction to predict etch removal amounts in recent cavity processes has shown to significantly improve the reliability of etching estimates in half-wave and quarter-wave resonators.

## CONCLUSION

The consistency of the experimental results is a promising sign, though the sample size of the data is relatively small. In order to determine with a high statistical probability the heat of reaction when BCP and niobium come into contact, many more trials should be performed. This statement is also true of the specific heat experiments. Experimental errors, including heat losses, environmental fluctuations, and faulty or insufficiently sensitive equipment can all impact the results of the experiment to a certain degree. By performing these experiments again, a greater degree of certainty in the data can be established. Despite the fact that further research is required, the results thus far suggest that the heat of reaction for these components is approximately -679 kJ/mol.

## ACKNOWLEDGMENTS

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