IODINE RETENTION ON STAINLESS STEEL

SAMPLING LINES

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

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ABSTRACT

In this study, deposition of I_{2(g)} on stainless steel tubing was investigated using radiochemical techniques. The purpose was to study the mechanisms of I_{2(g)} deposition on stainless steel sampling lines. I_2 deposits through both physical and chemical adsorption. Physical adsorption predominates at I_2 concentration below 10^{-9} mol/L. At concentration higher than 10^{-9} mol/L, slow chemisorption occurs for low humidity (<25%). At high relative humidity (>75%), rapid chemisorption with pitting corrosion occurs. I_2 is believed to react at defect sites to form hygroscopic FeI_2 which attracts more water propagating the reaction. Under some conditions the propagation is inhibited resulting in an apparent maximum surface loading. At high iodine concentration, high relative humidity and tube temperatures of 40° or 60°C, no such inhibition occurs resulting in rapid and continuous iodine adsorption.

Despite the expectation that SS-316L should perform better than SS-304L, there appears to be no difference between the two types of steel except, perhaps, at iodine concentrations below 10^{-9} mol/L.
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1. INTRODUCTION

1.1. General Overview

In the event of a core disruptive accident in a nuclear generating station, some fission products may be released from the fuel into the containment area. Among these fission products, radioiodine is one of the most important to consider in reactor safety studies.

Radioiodine causes great concern due to its high fission yield, its potential volatility and its radiobiological hazard. Some of the radioiodine released from the core may become airborne and escape to the environment. One of the most likely pathways of release from a multi-unit Candu (CANadian Deuterium Uranium) station is controlled venting through the Filtered Air Discharge System (FADS). Through its filtering capabilities, the FADS plays a very important role in minimizing the amount of radioactive fission products released to the environment. The concentration of gas phase iodine in the discharged air can be measured using the Post Accident Release Monitoring System (PARMS). The PARMS requires that the air samples be passed through a considerable length of stainless steel tubing to a remote location where the desired measurement can be safely made. A significant loss of iodine caused by adsorption on the sample line surfaces will greatly distort this measurement. The accuracy of the measurement is very important since it will be used to estimate the magnitude of any radioactive release. This information is needed to estimate the radiation dose to the population and, thereby, to determine appropriate off-site actions to protect the public.
1.2 The Role of Filtered Air Discharge System (FADS) and Post Accident Radiation Monitoring System (PARMS)

Should radioiodine escapes from the fuel, the last barrier before its release to the environment is the containment structure. The containment system of multi-unit CANDU reactors is maintained at sub-atmospheric pressure to prevent any uncontrolled radioactive emission to the outside air. Provided that this containment structure remains intact following any fuel failure, a major portion of the radioiodine will be safely kept within the containment building, or else be trapped by the FADS, hence minimizing the environmental impact of the incident.

The purpose of the FADS is to provide a filtered and well defined path for the controlled release of any air vented to the outside atmosphere. The FADS is not required under normal operating conditions. During normal operation, the FADS remains isolated from the reactor containment. It will be run following a substantial release of radioactivity into the containment area. Even so, it will only be operated when the pressure within the containment building is approaching atmospheric pressure. Once the required sub-atmospheric pressure is achieved, the FADS will be turned off. It will be turned-on and off subsequently to maintain the required low pressure inside the containment building.

To ensure high removal of fission products, the FADS has in place a series of filtering systems. For iodine removal, the system utilizes TEDA impregnated charcoal. This filter does have limits in its performance. Several factors that can affect the iodine filtering performance are the thermal stability of the organic charcoal impregnant (TEDA), the humidity of the influent gas as well as the flow rate of the gas [1]. Additionally, a small portion of iodine
which is already trapped in the charcoal bed may desorb. The amount of desorption will depend on the total iodine inventory on the filter [2].

Considering these limitations, it is necessary to monitor the amount of radioactivity that escapes to the atmosphere. The on-site measurement of radioactive release is crucial in estimating the amount of radiation dosage that may be received by the population especially by those within several kms of the reactor site. Additionally, the measurement results may also determine whether any off-site actions are required to protect the safety of the public. Therefore, it is crucial that the measurement be performed to a known degree of accuracy.

The activity in the released air is evaluated by the PARMS by sampling of the gas prior to the discharge point. A sampling port diverts some of the gas flow and carries it to a location where measurement can be safely made. A detection system is then used to detect and measure all of the major fission products that may be present in the gas stream. To carry the gas stream to the measurement point, the PARMS utilizes a length of stainless steel tubing. Steel type 304L is used in most of the existing systems. However, the 304L steel has recently been replaced by SS-316L at one of the plants.

Some species of gaseous iodine, such as I$_{2g}$, adhere to many materials. Stainless steel is not immune to this problem. As a result some of the radioiodine passing through the stainless steel tubing will deposit on the tubing surface before reaching the detection point. Because of this problem, the operator may be receiving misleading information regarding the amount of iodine being released from the reactor. The value reported may be lower than the actual amount of any release.
1.3 An Overview of the Study

Iodine released from the containment may be in many forms including $I_2(g)$, $CH_3I(g)$ and other organic iodides. $R_1I(g)$. However, of these, only $I_2(g)$ is readily adsorbed by steel. The objective of the study was to determine the effects of operating conditions on the deposition of iodine onto stainless steel tubing. The rate and extent of $I_2(g)$ deposition on two types of steel tubing was quantified and these results were applied to estimating line loses in existing PARMS systems. Possible mechanisms responsible for the retention were also proposed.

The operating conditions considered in this investigation included gas phase iodine concentration, relative humidity and tube surface temperature. Initially, it was anticipated that the rate of gas phase mass transfer would be dominant in determining the overall rate of iodine adsorption. As the project progressed, however, it became apparent that, given the proper conditions, the rate of surface reactions played a more important role. The operating conditions were expected to affect the rate of iodine deposition mainly through their effects on the interaction between iodine and metal constituents of the steel.

The experiments were performed by passing a gas stream containing $I_2(g)$ labeled with I-131 through 25.4 cm long, 1/4" OD, stainless steel tubing. The rate and extent of iodine retention were obtained by recording the gamma emission of any I-131 deposited on the tubing. Two types of steel were examined in this study, SS-316L and SS-304L. It was believed that, due to its metal composition, SS-316L would perform better in the presence of a reactive component such as molecular iodine, leading to lower iodine retention. Additionally, some experiments were also conducted on iodine deposition around stainless steel fittings. Iodine retention was expected to be high around the fittings.
In the beginning of this thesis, the published works of others that are relevant to the current project are summarized. These include some data on actual line testings performed by Ontario Hydro as well as some general characteristics of iodine interaction with stainless steel. The theories that are relevant to the process of iodine deposition are then presented. Following the theories, the experimental procedure used in the study is described. The discussion of results is then presented. The discussion focuses on the observed trends of deposition under various operating conditions as well as some possible mechanisms that can explain the behavior. The complete log of the experimental results can be found in the appendices. The relevance of the work to the general understanding of iodine/steel interactions and its applications to PARMS conclude the report. Based on the results, some recommendations for further studies are also given.
2. THEORETICAL CONSIDERATIONS

Iodine retention on the steel surface involves several distinct steps. The process begins with iodine being transferred from the gas phase to the tube surface. Once the iodine is on the surface it may be physically adsorbed and, considering the reactive nature of molecular iodine, it may then react with the metal constituents of the steel. Some of the iodine that is already deposited on the surface may become resuspended and be transferred back to the gas stream. These different phenomena will determine the rate and extent of iodine retention on steel sampling lines.

In this chapter, some theories that are relevant to the above processes are discussed. The equations that can be used to estimate the performance of sampling lines are also described.

2.1 Iodine Mass Transfer

The rate of iodine deposition will depend on two processes: deposition and desorption. It is therefore necessary to clearly define the terms related to these two phenomena. The parameter often used to describe the rate of iodine deposition is the deposition velocity, \( k_d \) (cm s\(^{-1}\)), which can be defined as follows:

\[
k_d = \frac{N_g}{C_g}
\]  

\( N_g \) = the iodine deposition rate (mol/cm\(^2\).s)

\( C_g \) = gas phase iodine concentration (mol/cm\(^3\)).
The iodine on the surface can also become resuspended and be transferred back into the gas stream. The constant that describes the rate of desorption is defined as follows:

\[ k = \frac{N_s}{C_s} \quad (2.2) \]

\( k \) = desorption rate constant \( (s^{-1}) \)

\( N_s \) = desorption rate \( (\text{mol/cm}^2 \cdot \text{s}) \)

\( C_s \) = iodine surface concentration \( (\text{mol/cm}^2) \).

Considering the above definition, the overall mass balance of iodine over the tube surface can then be set up:

\[ \frac{dC_s}{dt} = k_d C_g - kC_s \quad (2.3) \]

In Eqn. 2.3 it is implicitly assumed that the net iodine deposition rate is first order with respect to \( C_g \) as well as \( C_s \). Furthermore, this equation implies that after a certain period of iodine loading, steady state will be achieved. During such a condition, the rate of deposition would be equal to the rate of desorption. In the initial stage of deposition the iodine surface concentration should be very low. Consequently, the desorption term during this period will be negligible. Therefore, the initial deposition velocity can be estimated using the following equation.

\[ k_d = \frac{dC_s}{dt} \quad (2.4) \]

Eqn. 2.4 is used in this study to estimate the value of the initial deposition velocity.
2.2 Iodine Deposition Velocity

The process of deposition involves two distinct steps: gas phase mass transfer and iodine interaction with the steel surface. Consequently, the value of $k_d$ will depend on the two terms that are associated with these two separate steps. The rate at which iodine is transferred from the gas phase to the gas-surface interphase is denoted by $k_g$ while the rate at which the surface can receive or interact with the iodine is denoted by $k_s$. Mathematically, the relation between these parameters can be written as follow:

$$\frac{1}{k_f} = \frac{1}{k_g} + \frac{1}{k_s} \quad (2.5)$$

The process of deposition is illustrated in the following diagram.

---

Figure 2.1 Transfer of Iodine from the Gas Phase to the Tube Surface
Equation 2.5 above signifies that \( k_d \) cannot exceed \( k_g \) or \( k_s \). Furthermore, either \( k_g \) or \( k_s \) may be the term that will limit the overall deposition velocity. For example, if \( k_g \) is substantially larger than \( k_s \), then \( k_s \) will be the factor limiting the overall transfer of iodine and, consequently, will determine the value of \( k_d \). If the limiting step can be identified, effort to limit iodine loss along the sampling line can be accomplished by modifying the operating conditions so that this limiting step is further suppressed. Due to the importance of \( k_g \) and \( k_s \) in determining the overall rate of iodine deposition, the following sections are dedicated to discussing the two parameters.

### 2.3 Gas Phase Mass Transfer, \( k_g \)

The value of \( k_g \) can be estimated by using standard correlations based on the analogy with heat transfer. The dimensionless Sherwood number, \( Sh_g \), is used in the estimation.

\[
Sh_g = \frac{k_g D}{D_{th}} \quad (2.6)
\]

- \( D \) = tube inside diameter (cm)
- \( D_{th} \) = binary diffusion coefficient (cm²/s)

The Sherwood number can be estimated by using correlations for internal flow through a tube. The correlation that is applicable will depend on the type of flow within the tube. Two correlations to estimate the Sherwood number are presented below:

i) Fully developed laminar flow [3]:

\[
Sh_g = 4.36 \quad (2.7)
\]
ii) Combination of fully developed flow with entrance effect by Sieder and Tate [3]:

\[ Sh_f = 1.86 \left( \frac{Re_p Sc}{L D} \right)^{0.14} \left( \frac{\mu}{\mu_s} \right)^{0.14} \]  

\text{(2.8)}

Equation 2.8 is recommended by Whitaker if the condition below is satisfied

\[
\left( \frac{Re_p Sc}{L D} \right)^{0.14} \left( \frac{\mu}{\mu_s} \right)^{0.14} \geq 2
\]  

\text{(2.9)}

For the conditions relevant to the experiment, the term on the left is equal to 0.83. Thus, fully developed laminar condition encompasses much of the tube and, hence, equation 2.7 should be used.

- \( Re_p \) is the corresponding Reynolds number for flow through the tube:

\[
Re_p = \frac{\rho V D}{\mu} = \frac{V D}{\nu}
\]  

\text{(2.10)}

- \( Sc \) is the Schmidt number:

\[
Sc = \frac{\nu}{D_{\text{eff}}} = \frac{\mu}{\rho D_{\text{eff}}}
\]  

\text{(2.11)}

- \( D \) = tube diameter (cm)
- \( \rho \) = density (g/cm\(^3\))
- \( \nu \) = kinematic viscosity (cm\(^2\)/s)
- \( V \) = gas velocity (cm/s)
- \( \mu \) = viscosity of the gas (kg/m.s)
- \( \mu_s \) = viscosity of the gas near the wall (kg/m.s)

The viscosity of the gas near the tube wall, \( \mu_s \), can be estimated by the correlation of Shuterland [4]:
\[
\mu_s \left( \frac{kg}{m \cdot s} \right) = \frac{1.458 \times 10^{-6} T^2}{110.4 + T}
\]  
(2.12)

\( T \) = temperature in Kelvin

To obtain kinematic viscosity from \( \nu = \frac{\mu_s}{\rho} \), the dynamic viscosity, \( \mu_s \), can be estimated by Eqn. 2.6 above while the density of air can be estimated by using the ideal gas law. For comparison, some plotted values of kinematics viscosity by Fox et.al. can be used [4].

The estimation of binary diffusion coefficient, \( D_{AB} \), is more complicated compared to any other variables involved. There are several methods available to estimate \( D_{AB} \). The difficulty is that some of the data required are not available in the literature. For the purpose of this study, a simple correlation by Fuller, Schettler and Giddings was used [5]. The equation is as follow:

\[
D_{AB} = \frac{10^{-4} T^{\frac{4}{3}} \left[ (M_A + M_B) \left( \frac{M_A M_B}{M_A + M_B} \right)^\frac{1}{3} \right]}{P \left( \frac{\Sigma v_A}{3} + \left( \frac{\Sigma v_B}{3} \right) \right)^\frac{1}{3}}
\]  
(2.13)

\( D_{AB} \) = binary diffusion coefficient \((cm^2/s)\)
\( M_A \) and \( M_B \) = molecular weight of component A and B
\( T \) = bulk temperature in Kelvin
\( P \) = pressure in atmosphere
\( \Sigma v_A \) and \( \Sigma v_B \) = the atomic diffusion volumes of component A and B

2.3.1 The Effects of Temperature on k_g

In the current investigation, tube surface temperature is one of the main variables being studied. The variation in temperature is expected to have some impact on the rate of gas phase mass transfer by altering the values of \( \mu_s, \nu, D_{AB} \). These parameters, however, are only weakly
affected by variations in temperature within the range relevant to the current investigation. Hence, the rate of gas phase mass transfer can be expected to be affected only marginally. The following table shows the impact of increasing gas temperature on the value of $k_g$. For the purpose of calculating viscosity, a mean value of tube surface temperature and temperature of the gas was used.

Table 2.1 Effect of temperature on $k_g$

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$k_g$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>0.73</td>
</tr>
<tr>
<td>40</td>
<td>0.77</td>
</tr>
<tr>
<td>60</td>
<td>0.81</td>
</tr>
<tr>
<td>90</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The combination of temperature and relative humidity on $k_s$ is more important to consider and this is discussed in chapter 3.

2.4 Iodine Interaction with Steel

Unlike $k_g$, it is very difficult to estimate $k_s$ based on any mathematical expression. There are various phenomena involved in the determination of $k_s$ such as temperature and relative humidity along with their impact on the growth and disappearance of water films or water droplets on the surface during an experiment. As described in chapter 3, it is possible that $k_s$ plays a very important role in determining the overall $k_d$. 
In the sections below, some possible interactions between iodine and steel surface are discussed. The phenomena described should assist the interpretation of the data obtained from the experiments.

2.4.1 Physical adsorption

After iodine is transferred to the steel surface, there are two possible types of interaction between the iodine molecules and the steel surface. The first is physical adsorption of the molecular iodine. Physical adsorption involves weak or indirect bonding between the iodine molecules and the steel surface. Given that the bond is not to any specific atom on the surface, physical adsorption is not usually limited by the number of reaction sites on the surface. However, as iodine layers near the surface increase, the bonding force becomes progressively weaker, due to the increased distance from the surface. In fact, physical adsorption beyond monolayer coverage does not usually occur unless the partial pressure of the adsorbate is close to its vapour pressure. After a certain period of loading, a balance between the attractive force of the surface and the repulsive force created by the concentration gradient between the surface and the bulk will be achieved. Hence, the surface will achieve a steady state. As a result, the deposition velocity is initially high but declines as deposition proceeds, reaching zero at steady state. Some authors have reported that monolayer coverage of a steel surface is on the order of \(10^{-9}\) mol/cm\(^2\) [6]. Deir, however, observed maximum loadings up to \(10^{-7}\) mol/cm\(^2\) [7]. This suggests that hundreds of monolayer adsorbed onto the steel surface or that the deposition was not due to physical adsorption alone.
The second process is iodine adsorption that involves chemical reactions. The process is also commonly known as chemisorption. The process of chemisorption is usually preceded by physical adsorption. Several authors such as Deir and Tsukaue et.al [7.8.9] have proposed interactions which involve pitting corrosion attack of steel by iodine. A scheme involving corrosion reactions were suggested since, as described in chapter 3, direct reaction between I$_2$ and Fe will not occur to any appreciable extent at temperatures lower than 200°C [6]. The possible chemical reactions will be elaborated in the following subsections.

2.4.2 Pitting corrosion of Steel by Iodine

Pitting is a highly localized corrosion attack on a metal surface while leaving most of the metal surface intact. The attack may begin on a site where the protective oxide film has been damaged. Certain anions such as halides, most notably chlorides, are known to be capable of damaging the oxide layer [10.11]. Corrosion pitting due to bromide, fluoride as well as iodide has also been observed [8.9.11]. Other important factors that may increase the probability of pitting attack are impurities such as the inclusion of manganese sulfide [9], temperature and relative humidity [8.9.11]. Addition of alloying metal such as molybdenum into the stainless steel has been known to reduce pitting probability.

In relation to iodine retention along stainless steel sampling lines, the involvement of pitting corrosion may enable the steel surface to accumulate a higher amount of iodine than if merely physical adsorption were occurring. It is likely, for example, that the high iodine accumulation observed by Deir involved a combination of physical adsorption and chemisorption.
The chemical reactions involved in the process are electrochemical in nature. The presence of water is necessary for the reaction to occur. Deir has suggested some of the key reactions that may be involved in steel attack by iodine [7]. These reactions are described below.

\[
\begin{align*}
\text{Fe}^{2+}_{(aq)} & \leftrightarrow 2\text{e}^- \leftrightarrow \text{Fe}_{(s)} \quad (-0.44 \text{ V}) \quad (R \ 2.1) \\
\text{I}_2(g) & \leftrightarrow 2\text{e}^- \leftrightarrow 2\text{I}^- \quad (+0.536 \text{ V}) \quad (R \ 2.2)
\end{align*}
\]

Combining the two equations yields:

\[
\text{Fe}_{(s)} - \text{I}_2(g) \leftrightarrow \text{Fe}^{2+}_{(aq)} - 2\text{I}^- \quad (+0.976 \text{ V}) \quad (R \ 2.3)
\]

The resulting Fe\(^{2+}\) ions may react with O\(_2\) diffusing from the gas phase under the presence of water giving the final corrosion products Fe\(_2\)O\(_3\):

\[
4\text{Fe}^{2+}_{(aq)} + \text{O}_2 + (4 + 2x)\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}_{(s)} + 8\text{H}^+ \quad (R \ 2.4)
\]

The iodide ions will also react with the molecular iodine resulting in the formation of triiodide ions.

\[
\text{I}_2(g) - \text{I}^- \leftrightarrow \text{I}_3^- \quad (R \ 2.5)
\]

Triiodide ions are very reactive and it may contribute to further corrosion of the steel [7]. The following diagram illustrates one possible scheme of stainless steel attack by molecular iodine diffusing from the gas phase.
2.5 Estimation of Iodine Transmission Fraction

Upon obtaining the data for rate and extent of iodine retention under various experimental conditions, it is important that these data be related to the performance of existing gaseous iodine sampling lines. For the purpose of estimating the transmission fraction, a simple correlation that involves deposition velocity can be used. The equation is based on the rate of change of iodine molar flow rate through the steel tube. It assumes that the deposition rate is proportional to the iodine concentration. Due to these assumptions, the equation may only be applicable over a short period of time which will depend on several factors. One of the most important factors is the iodine gas phase concentration. For example [12], during an accident with $C_g$ near $10^{-6}$ mol/L and a relatively high deposition velocity of 0.1 cm/s, the time required to reach saturation would be up to several days. A similar time frame is required until desorption rate becomes significant. However, it can be expected that the actual $k_d$ during an
accident would be lower than 0.1 cm/s. This will increase the period of applicability of the equations. The equation is as follows.

\[ F \times dC_g = -C_g \times \pi \times D \times k_d \times dx \quad (2.14) \]

Separating the variable and integrating:

\[ \int_{C_g_0}^{C_g} \frac{dC_g}{C_g} = -\frac{\pi \times D \times k_d}{F} \int_0^L dx \quad (2.15) \]

iodine transmission fraction (t) = \[ \frac{C_{g_x}}{C_{g_o}} = \exp\left(-\frac{k_d \times \pi \times D \times L}{F}\right) \quad (2.16) \]

The equation can also be written by using gas linear velocity (V) to replace gas volumetric flow rate (F), yielding:

iodine transmission fraction (t) = \[ \frac{C_{g_x}}{C_{g_o}} = \exp\left(-\frac{4 \times k_d \times L}{V \times D}\right) \quad (2.17) \]

\( C_{g_0} \) = iodine gas phase concentration at inlet (mol/cm³)
\( C_{g_o} \) = iodine gas phase concentration at outlet (mol/cm³)
\( k_d \) = deposition velocity (cm/s)
\( F \) = volumetric flow rate (cm³/s)
\( L \) = line length (cm)
\( D \) = tube inside diameter (cm)
\( V \) = gas linear velocity (cm/s)

As stated previously, the equation neglects the rate of desorption as well as the declining value of \( k_d \) with time due to saturation. Both factors will improve transmission fraction. Therefore, the equation is likely conservative and it should overestimate the loss over the long term. However, the equation also does not consider any increase in \( k_d \) with increasing surface loading as a result of corrosion or other surface reactions. Hence it is possible that this equation will underestimate the loss under some conditions.
3. LITERATURE SURVEY

Extensive studies have been carried out to investigate the performance of radioiodine monitoring systems in nuclear reactors. These studies include on-site tests at nuclear stations and experiments performed in laboratories. Some of the investigations which have been directed toward assessing and improving the reliability of existing radioiodine sampling systems, as well as improving the current understanding of iodine interaction with stainless steel surface, are also discussed in this chapter.

There are various parameters that can be used to characterize the performance of radioiodine sampling lines. In the sections to follow, the effects of these parameters on the rate and extent of iodine retention are described. The parameters are discussed in the following order: iodine species distribution, tube diameter and length, volumetric flow rate, iodine gas phase concentration, interaction of iodine and steel along with the effects of temperature and relative humidity, the type of material used in the sampling line and several other factors such as fittings, bends and cleaning of the sample line.

3.1 Iodine Species Distribution

Iodine species distribution in reactor effluent is of interest because iodine transport behavior through sampling lines is highly dependent on the iodine forms. An average iodine species distribution from three Pressurized Water Reactors (PWRs) and three Boiling Water Reactors (BWRs) is given in table 3.1 [13]. These values will not necessarily be applicable to any specific plant as the distribution and quantity will differ amongst plants, plant areas and different operating modes.
Table 3.1 Iodine species distribution in PWRs and BWRs [13]

<table>
<thead>
<tr>
<th>Radioiodine Species</th>
<th>PWR (%)</th>
<th>BWR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Iodine (I₂)</td>
<td>27</td>
<td>28</td>
</tr>
<tr>
<td>Hypoiodous acid (HOI)</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Organic Iodides (CH₃I, etc.)</td>
<td>31</td>
<td>40</td>
</tr>
<tr>
<td>particles</td>
<td>2</td>
<td>12</td>
</tr>
</tbody>
</table>

Among these iodine species, I₂ is the most reactive and, as a consequence, it presents the biggest challenge to design engineers due to its high retention on the surface of sampling lines. Unrein et al. reported that the deposition velocity (k_d) of HOI is less than 5% of that for I₂ while the deposition velocity of CH₃I is less than 0.1% of that of I₂ [14]. Glismeyer and Sehmel also observed similar behavior for I₂, HOI and CH₃I [13]. Tests performed by Ontario Hydro during the year 1992 and 1993, at Bruce NGS-B stack monitor and Pickering PARM system, showed a similar trend. Negligible retention of CH₃I was found even though significant retention of I₂ was observed within these lines [15,16]. Due to its greater retention, much more attention has been paid to investigating I₂ transport behavior through stainless steel sampling lines.

The current research deals only with I₂. In the following sections, only literature data that pertain to the transport behavior of I₂ are presented. Data regarding the other iodine species are included only if they are relevant to the discussion.

3.2 Tube Inside Diameter and Length

The impact of tube diameter on retention has usually been studied in conjunction with flow rate. For this reason, the discussion in this section will be closely related to the discussion on the effect of flow rate within the next section.
Experiments have been performed with stainless steel tubes with different sizes and lengths. The length of the tube varied from as short as 15 cm to as long as 78 m, while the tube diameter was varied from 0.457 cm to close to 2.54 cm (1”). Some experiments have also been performed with stainless steel coupons. In this section, only results with steel tubing are presented.

Unrein et al. [14] performed experiments at temperatures between 25°C to 30°C with relative humidities between 25% to 70%. The steel used was either SS-304 or SS-316. There is no specific mentioning which steel type was used in any particular line. The difficulties with the data is that the tube diameter was varied together with gas volumetric flow rate. Both parameters would play their roles in determining the transmission fraction of iodine. As a result, it is difficult to determine whether the tube diameter or the flow rate was the predominant effect.

Table 3.2 Effect of tube inside diameter on transmission fraction [14]

<table>
<thead>
<tr>
<th>Line #</th>
<th>Inside Diameter</th>
<th>Length (m)</th>
<th>Flow rate (L/min)</th>
<th>Velocity (m/s)</th>
<th>(A/V) ratio (cm⁻¹)</th>
<th>Transmission Fraction</th>
<th>k_d (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.22 cm</td>
<td>30.48</td>
<td>84.96</td>
<td>3.66</td>
<td>1.80</td>
<td>75%</td>
<td>0.020</td>
</tr>
<tr>
<td>2</td>
<td>2.22 cm</td>
<td>15.24</td>
<td>84.96</td>
<td>3.66</td>
<td>1.80</td>
<td>78%</td>
<td>0.032</td>
</tr>
<tr>
<td>3</td>
<td>1.91 cm</td>
<td>42.93</td>
<td>56.64</td>
<td>3.30</td>
<td>2.10</td>
<td>23%</td>
<td>0.054</td>
</tr>
<tr>
<td>4</td>
<td>1.91 cm</td>
<td>42.93</td>
<td>56.64</td>
<td>3.30</td>
<td>2.10</td>
<td>62%</td>
<td>0.018</td>
</tr>
<tr>
<td>5</td>
<td>0.64 cm</td>
<td>42.67</td>
<td>1.70</td>
<td>0.88</td>
<td>6.30</td>
<td>0.13%</td>
<td>0.027</td>
</tr>
<tr>
<td>6</td>
<td>0.64 cm</td>
<td>42.67</td>
<td>1.70</td>
<td>0.88</td>
<td>6.30</td>
<td>0.45%</td>
<td>0.021</td>
</tr>
<tr>
<td>5</td>
<td>2.21 cm</td>
<td>78.03</td>
<td>56.64</td>
<td>2.46</td>
<td>1.81</td>
<td>58%</td>
<td>0.0095</td>
</tr>
<tr>
<td>6</td>
<td>2.12 cm</td>
<td>74.98</td>
<td>79.26</td>
<td>3.45</td>
<td>1.89</td>
<td>72%</td>
<td>0.0088</td>
</tr>
</tbody>
</table>

Based on the data above, the variation in tube diameters and flow rates does not appear to influence the rate of mass transfer of iodine to the tube surface. No significant changes in deposition velocity was observed. This is somewhat surprising since a decrease in gas linear velocity accompanied by a lower value of tube diameter, such as shown in line 4 in table 2.2.
should decrease the Reynolds number which should reduce the gas phase mass transfer coefficient. It is likely that, given the low values of $k_d$, gas phase side mass transfer was not the limiting factor, or the change in flow conditions was not sufficient to alter the deposition velocity.

The transmission fraction, however, suffers a substantial decline in line no. 4. Compared to the other lines, this line has the smallest tube size (0.64 cm) as well as the lowest linear gas velocity (0.88 cm/s). The reduction in transmission fraction is expected since the tube size and gas linear velocity were reduced. Smaller tube diameter means higher surface area to volume ratio while lower linear velocity means higher residence time. Both will enhance the opportunity for interaction between iodine and the steel surface.

Deir performed experiments under similar conditions as the ones in line no. 4 and obtained higher values of $k_d$ ranging from 0.07 cm/s to 1 cm/s [17.7]. One possible difference is the gas concentration which may have been much lower in the experiments of Unrein et.al. Unfortunately, gas concentration was not reported by Unrein et.al..

### 3.3 Volumetric Flow Rate

Flow rate is expected to influence $I_2$ retention by affecting the rate of mass transfer. Gas phase side mass transfer may play a very important role in determining the rate of $I_2$ deposition since prior to any interaction between $I_2$ and the steel surface, the $I_2$ must first be transferred to the surface from the gas phase. The gas flow rate will also affect $I_2$ retention by changing the residence time. This will be discussed in the section on interaction of $I_2$ with a stainless steel surface.
In some experiments performed at low flow rate by Deir, it was shown that when the flow was increased by two, there was a possible impact on the deposition velocity [7]. The tube diameter was 0.64 cm and the length was 15 cm. Even though the experiment was performed in the laminar region, compared to results from other researchers, the deposition velocity was found to be very high. End effects may be dominant in this case. The values are slightly higher than 1 cm/s.

Table 3.3 Effect of flow rate on deposition velocity (SS-316L) [7]

<table>
<thead>
<tr>
<th>Flow Rate (L/min)</th>
<th>Temp (°C)</th>
<th>%RH</th>
<th>$[I_2]_g$ (mol/L)</th>
<th>$k_d$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>23</td>
<td>30</td>
<td>$2 \times 10^{-9}$</td>
<td>1.15</td>
</tr>
<tr>
<td>2.3</td>
<td>24</td>
<td>63</td>
<td>$8 \times 10^{-9}$</td>
<td>1.12</td>
</tr>
<tr>
<td>3.2</td>
<td>24</td>
<td>49</td>
<td>$7 \times 10^{-9}$</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Experiments with similar tube size and flow rate have been performed by Genco et.al. [19]. Genco et.al. carried out the experiments at temperatures above 150°C. Such temperature is too high to be applicable to a radioiodine sampling line. Most sampling lines operate at temperature between ambient to 50°C [13]. The experiment was originally intended to study iodine deposition on the primary heat transport system.

The tube used was 137 cm long. This length is sufficient to suppress the end effect on the overall deposition velocity. Additionally, the tube had been presized by exposing it for 1000 hours to water at 288°C recirculated at a flow rate of 8 m/s. At the above conditions, the observed value of $k_d$ was much lower, ranging between $10^{-4}$ cm/s under dry conditions to $10^{-3}$ cm/s when the air was mixed with steam (10% v/o). A 40 m long sampling line operated with this deposition velocity would, in theory, have a transmission fraction of approximately 90%.
Edson et al. carried out some experiments at a high flow rate of 187 L/min (linear velocity = 835 cm/s) with an iodine gas phase concentration in the order of $5 \times 10^{-10}$ mol/L [18]. This flow rate is approximately 2 to 3 times higher than the flow rate generally used by other researchers. The tube size was 2.18 cm while the length was 45.72 m. Provided that deposition velocity is on the order of $10^{-2}$ cm/s or lower, at this combination of tube diameter and gas linear velocity, a high transmission fraction would be expected. A relative humidity of 50% and temperature of 30°C were chosen as there was no available literature value for the predicted temperature and relative humidity during postulated accident conditions. The values of $k_d$ tabulated below are calculated based on the observed transmission fraction.

Table 3.4: Transmission fraction at high flow rate [18]

<table>
<thead>
<tr>
<th>Flow Rate (L/min)</th>
<th>%RH</th>
<th>$k_d$ (cm/s)</th>
<th>$T$ (°C)</th>
<th>Transmission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-304</td>
<td>187</td>
<td>50</td>
<td>$4.6 \times 10^{-2}$</td>
<td>30</td>
</tr>
<tr>
<td>SS-304</td>
<td>187</td>
<td>50</td>
<td>$5.1 \times 10^{-3}$</td>
<td>30</td>
</tr>
</tbody>
</table>

It should be noted that the loading after four hours would have been less than $10^{-9}$ mol/cm². It is shown in this thesis that at these low loadings, deposition due to chemisorption is not usually significant. Another observation made by Edson et al. was that the transmission fraction was lower during the initial period compared to the value obtained at the end of the 4 hour experiment. No explanation was offered for the phenomenon. Deir mentioned that after a period of deposition, the rate of deposition declines and eventually a maximum loading can be reached [7]. This suggests that there is a limit in the number of sites available for iodine adsorption or that the system approaches steady state. As a result, the deposition velocity may decrease as iodine deposition proceeds.
Edson et al. also included a plot of iodine transmission as a function of flow rate as reported by Widner et al.. The data demonstrates the sensitivity of iodine transmission fraction especially at very low flow rates. The basis of the data was a stainless steel line with 0.64 cm (0.25") inside diameter, 46 m long and a deposition velocity of 0.023 cm/s.

![Figure 3.1: Initial Iodine Transmission as a Function of Flow Rate [18]](image)

Based on the data presented in the last two sections, it may be possible to attain a value of deposition velocity in the order of 10^{-2} cm/s or lower. If this can be consistently maintained, it is then possible to achieve transmission fraction of 80% or higher by selecting a proper combination of flow rate and tube diameter. Based on the data discussed previously, small tubing such as 0.64 cm and low linear gas velocity should be avoided. An example of such situation can be found at high activity monitoring system at the Pickering NGS PARMS [16]. The design flow rate used is 1.7 L/min (88 cm/s) which is very low. Based on some tests performed by Ontario Hydro, the transmission fraction obtained is between 1% to 18%. Ontario Hydro tests results will be discussed further in a separate section.
The value of deposition velocity, however, may be a stronger function of other operating conditions such as I₂ gas phase concentration, temperature and relative humidity. These operating conditions may be more difficult to control since they depend on the atmospheric conditions within the containment building. These parameters may affect the deposition velocity by altering the nature of the interaction between iodine and the steel. This is discussed in the following sections.

3.4 Iodine Gas Phase Concentration

There have been few researchers who have investigated iodine retention with gas phase iodine concentration as one of the main parameters. One of the most extensive data sets was obtained by Deir [7,17]. The experiment was divided into two categories, low gas phase concentration and high gas phase concentration. The low gas phase concentration experiment ranged between 10⁻⁹ mol/L and 4x10⁻¹¹ mol/L while the high gas phase concentration ranged from 10⁻⁷ mol/L to 8x10⁻⁹ mol/L. The tube test samples were 15 cm long pieces of SS-316L tubing with a 0.64 cm outside diameter.

Based on the results of Deir, it appears that deposition velocity is less sensitive to variation in gas phase concentration than to a combination of temperature and relative humidity. Generally, the values are on the order of 0.1 cm/s or higher. At high gas phase concentrations, temperatures higher than 70°C and low humidity, the deposition velocity decreased to between 2x10⁻⁴ cm/s and 10⁻³ cm/s.

An additional observation made by Deir is that at high gas concentrations, saturation values for the iodine surface concentration exist. He suggests that there may be a limited number
of adsorption sites such that the deposition velocity is high in the beginning and continuously declines as the experiment proceeds. Eventually, the amount of deposited iodine reached its maximum value. This may explain the phenomena observed by Edson and Duce [18]. They found that during the first 15 minutes, the transmission factor was as low as 63%. At the end of 4 hours, however, the transmission fraction was raised to 95% or higher.

Morris and Nichols performed some experiments under similar conditions [20]. At a high gas phase concentration, 20°C and low humidity they obtained a deposition velocity of 0.12 cm/s which is similar to values obtained by Deir. At a low gas phase concentration they found that deposition velocity decreased to 0.048 cm/s. A similar trend was observed at an elevated temperature of 150°C. At this temperature, the high gas phase concentration yielded a deposition velocity of 3.6x10^{-2} cm/s while at the low gas phase concentration, the deposition velocity was reduced to 9.1x10^{-3} cm/s. According to the data obtained by Morris et.al., lowering the gas phase concentration may also lower the deposition velocity. Results by Deir, however, point out that the effect of temperature and relative humidity may be more significant.

### 3.5 Iodine Interactions with the Steel Surface

In this section, the nature of iodine interaction with stainless steel surface along with its possible consequences on the rate and extent of iodine retention are discussed. Since the phenomena may be strongly affected by temperature and relative humidity, these parameters are also considered in the current section.

After the iodine is transferred from the gas phase to the tube surface, it may be physically adsorbed to the steel surface and it may undergo chemical transformation due to reactions that
occur with the metal constituents of the stainless steel. Iodine that undergoes these reactions may be irreversibly bound to the metal surface. Below is some data obtained from exposing Cr, Ni and Fe to gaseous iodine. The three metals are the major constituents of stainless steel. The absence or presence of desorption may indicate the nature of iodine interaction with the steel.

Table 3.5 Iodine deposition on Fe, Cr, and Ni at temperature around 388 K (115 °C) [6]:

<table>
<thead>
<tr>
<th>Hours of Exposure</th>
<th>Iodine mg/cm²</th>
<th>Desorption under dry/damp air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 18</td>
<td>10⁻⁶</td>
<td>No desorption in damp air observed</td>
</tr>
<tr>
<td>Ni 18</td>
<td>0.146</td>
<td>No desorption observed</td>
</tr>
<tr>
<td>Fe 24</td>
<td>6</td>
<td>Desorption in dry air was observed. 0.45 mg/cm² was irreversibly bound</td>
</tr>
</tbody>
</table>

Based on these data, desorption from Cr and Ni could not be induced. This suggests that the iodine may be chemically bound to these metals in steel. Desorption of iodine from the iron surface, on the other hand, could be induced though approximately 7.5% of the amount deposited could not be desorbed. It is possible that some of the iodine may have reacted with the iron while some was merely physically adsorbed onto the metal surface. Given the much higher loadings as compared to Ni and Cr, the results suggest that Fe should be the largest sink for iodine among the metal constituents of steel.

Chemical reactions between iodine and stainless steel will produce metal iodides. The formation of iodide molecules on the steel surface has been observed by Tyler et.al. after exposing the steel surface to gas containing a mixture of CO₂/CH₃I [21,22]. These investigations, however, did not suggest any specific chemical reactions that could produce the iodide. Abrefah et.al. also found that the deposited iodine is chemically bound to the steel surface [23]. Hellmann and Funke found that direct elemental reactions between I₂ and stainless steel could only occur at
temperatures higher than 200°C [24]. Data presented in table 2.5 was obtained at lower temperature. Therefore, such direct reactions could not have been responsible for the value obtained. Several authors such as Deir [7] and Tsukaue et al. [8,9] have suggested a mechanism involving corrosion reactions. Fukuda et al. also investigated corrosion reactions of steel by iodine except that they carried out experiments at very high temperature [25]. Interestingly, Fukuda et al. also found that irradiation would make the steel more prone to corrosion attack. The reason is that the exposure to radiation could damage the oxide layer that initially protects the stainless steel.

3.5.1 Effect of Temperature and Relative Humidity

A corrosion reaction is electrochemical in nature and would require the presence of water on the surface of the tubing. It should therefore be expected that higher gas water content will assist the process. Furthermore, it is also possible that increasing the temperature will also accelerate the corrosion process. Deir [7] found that increasing the tube temperature to 40°C at high humidity increased the rate of iodine retention. However, when the temperature was raised to above 70°C, the rate of retention was substantially lowered. Deir suggested that at this condition the availability of water on the tube surface was significantly reduced and, as a result, the reaction could not proceed.

Genco et al. and Abrefah et al. also found that the rate of iodine retention was increased in an air-steam environment [19, 23]. Lee and Jester also carried out some experiments under different relative humidities and ambient temperature[26]. At higher relative humidity, the rate of
retention or deposition velocity was higher. Morris and Nichols also observed a similar increase of iodine deposition at high relative humidity [20].

The above relationship between temperature or relative humidity and the deposition velocity supports the theory of increasing iodine retention due to corrosion attack of the stainless steel. Tsukaue et.al. have investigated such attack on stainless steel coupons [9]. In these experiments, the stainless steel coupons were exposed to a gas flow containing I₂ under high humidity conditions. They observed that pitting corrosion occurred on the steel surface. The corrosion attack began on several active sites. From these initiation points, the reactions only propagated some of the time. A delay period, or incubation time, was observed before the corrosion reaction proceeded.

Some factors that can affect the propagation of corrosion are the existence and growth of water droplets or films on the metal surfaces, diffusion of iodine into the droplets or films and evaporation or resuspension of iodine from this small amount of water. Therefore, the operating conditions such as temperature, relative humidity, flow rate and iodine gas phase concentration can influence iodine retention by affecting the above phenomena. Additionally, temperature and relative humidity may also influence iodine retention rate by increasing the rate of any corrosion reactions that may occur. The impact of these complex phenomena on iodine retention rate have not been studied thoroughly.

Tsukaue et.al. also observed that one of the consequences of the corrosion reactions was the formation of triiodide molecules (I₃⁻) [8,9]. Triiodide could be formed by the reaction between I₂ diffusing from the gas phase with the I⁻ created on the steel surface through the chemisorption process. The presence of water is required for the reaction to occur. Triiodide is
corrosive in nature. Thus it may increase the rate of corrosion of the steel. Higher temperature
and higher relative humidity may serve to accelerate the reactions as well. Very high
temperatures, however, may reduce the amount of surface water and consequently the extent of
the chemical reactions.

Corrosion attack by iodine may introduce further consequences. Elemental iodine in the
water phase that attacks steel surfaces should be converted into non-volatile iodides (I\(_2\)). These
iodides are highly soluble in water and immediately dissolve. As a result the same steel surface is
available for further attack by iodine. Therefore, it is possible that the sequence of the corrosion
reactions will cause the steel to be capable of adsorbing a higher amount of iodine than if simple
physical adsorption was occurring on the surface.

3.6 Steel Type: SS-304 and SS-316

During 1989 Ontario Hydro investigated the necessity of replacing the existing SS-304
sampling line with SS-316L [27]. It was expected that iodine retention could be reduced by this
change.

Table 3.6 Metal composition of SS-304L and SS-316L [28](a):

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>304L</strong></td>
<td>0.014</td>
<td>0.60</td>
<td>1.2</td>
<td>0.036</td>
<td>0.007</td>
<td>18</td>
<td>10</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td><strong>316L</strong></td>
<td>0.015</td>
<td>0.66</td>
<td>0.8</td>
<td>0.032</td>
<td>0.001</td>
<td>17</td>
<td>12</td>
<td>2.1</td>
<td>Balance</td>
</tr>
</tbody>
</table>

(a) Composition may vary depending on the manufacturer.

Both types of steel have high chromium content. It is generally known that the existence
of CrO\(_2\) on the steel surface provides the steel with its stainless quality and, therefore, protects
the main body of the steel against any chemical attack from the outside environment. The main
difference between SS-316 and SS-304L is the high molybdenum content in SS-316L. High molybdenum content in SS-316L adds to its superiority against pitting as well as crevice corrosion attack. There have been a number of studies showing the good corrosion resistance property of steel with high molybdenum content [29, 30, 31].

Despite the superior property of SS-316L, there is no data to support its better performance when the material is used in a radioiodine sampling system. Lee and Jester performed experiments with both types of steel, under various levels of relative humidity at ambient temperature.

Table 3.7 Iodine deposition velocity on SS-316L and SS-304L sampling lines [32]:

<table>
<thead>
<tr>
<th></th>
<th>Flow Rate (L/min)</th>
<th>%RH &lt; 20%</th>
<th>50% &lt; %RH &lt; 70%</th>
<th>%RH &gt; 80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-316L - #1</td>
<td>65.1</td>
<td>8x10^-2</td>
<td>3.8x10^-2</td>
<td>4.5x10^-3</td>
</tr>
<tr>
<td>SS-316L - #2</td>
<td>65.1</td>
<td>2x10^-2</td>
<td>5x10^-2</td>
<td>1x10^-2</td>
</tr>
<tr>
<td>SS-304L</td>
<td>65.1</td>
<td>6x10^-2</td>
<td>1.2x10^-2</td>
<td>1.8x10^-3</td>
</tr>
</tbody>
</table>

NOTE: high [I\(_2\)]\(_g\) = 6.25x10^-8 mol/L, high flow: 65.1 L/min (most tests), ambient temperature 2.29 cm ID (0.90" ID), L = 6.096 m, (sur)face/volume\(_\text{ratio}\) = 1.78 cm\(^{-1}\)

Based on the results above, SS-304L performed better than SS-316L at all the relative humidities examined. This is contrary to what is expected. A rationalization of the phenomena could relate to the low temperature at which the experiment was executed. At ambient temperature, it appears that both SS-304L and SS-316L are able to maintain their stainless quality such that only a relatively low amount of iodine can be deposited. This, however, does not rule out the possibility that corrosion reactions take place to some extent. The inability of the corrosion to propagate may have prevented the steel from becoming a large iodine adsorber.
The effects of temperature is crucial since many iodine sampling lines have trace heating systems. The purpose of the heating is to prevent freezing of the lines, as well as to prevent water condensation along the lines [13]. Most sampling lines operates at a temperature between ambient and 50°C. The trace heating may in fact have a negative impact on the amount of iodine losses. Higher temperature may increase steel susceptibility to corrosion attack. Under these conditions, it is possible that a higher content of molybdenum would increase the protection against corrosion attack, and hence SS-316L would have lower retention than SS-304L.

Tsukaue et.al. have carried out some experiments at 60°C and relative humidity approaching 100% [9]. Their results showed that even at this elevated temperature, there is no clear difference in the rate of pitting corrosion propagation between SS-304L and SS-316L. In some instances, SS-316L appeared to be more susceptible to corrosion attack as compared to SS-304L. The necessity of further research to justify the replacement of SS-304L with SS-316L is noted.

3.7 Other effects

Several investigators have indicated that there could be several other factors which would affect the rate and extent of iodine retention on steel sampling lines. These factors include the number of fittings and bends in the sampling system as well as pretreatment of the steel tubing prior to installation.
3.7.1 Fittings and Bends

Fittings and bends are locations along the sampling line where the flow configuration might change. A higher level of turbulence may be induced around these regions. As a result, deposition of iodine may be increased due to a higher mass transfer rate. Several authors such as Genco et.al [19] and Edson et.al. [6] have observed higher level of iodine retention around compression fittings. Genco et.al. further suggested that the main cause of this increased iodine retention was damage of the oxide films as a result of cutting of the tubing. Genco et.al. also added that stress caused by compression fittings may increase iodine retention. To test this hypotheses, Genco et.al. placed screw-type hose clamps at two locations along the tubing. They observed higher iodine retention at the points where the clamps were tightened. Visual examinations also revealed a localized black deposit beneath the clamp thus confirming their hypotheses. Therefore, it may be crucial that during the design process attention is given to the number of fittings and bends between the sampling and the measurement points.

3.7.2 Cleaning the sampling Lines

Cleaning of the sampling lines may affect the extent of iodine retention. Some contaminants that exist inside the tubing may interact with the iodine from the gas phase; thus causing higher retention rate. Lee and Jester found that when the tube was used as received, there were some points where iodine deposition was substantially higher than any other region within the tubing [26]. Upon cleaning, this localized high iodine deposition disappeared.
Edson et al. however obtain different result [18]. They found that cleaning had little to no effect on the amount of iodine retention. The differences in result may suggest that the contaminant may be specific to tubing from a particular tubing manufacturers.

The operating history of a sampling line may also affect its performance. Some foreign objects such as charcoal filter particles or any filter material fragments may be entrained during any regular tests or during normal operations. This may cause high localized iodine retention. Regular cleaning of the line is recommended.

3.8 Tests at Ontario Hydro

A significant number of tests have been performed by the Ontario Hydro at all three of its nuclear power stations. Most tests involved three species, namely uranine particulates, molecular iodine vapor and methyl iodide. The results from these tests have been mixed. Some tests showed excellent iodine transmission factors but some did not. During the tests, temperature and relative humidity were not controlled or measured. Ambient temperature and relative humidity must therefore be assumed.

Part of these tests were performed at the exhaust stack monitoring system. These are the stacks through which any radioactive gases and particulates are released during normal operation. In an accident conditions, any release should occur through the EFAD systems. Therefore, some of the tests were also performed for the PARMs monitoring systems. Tests performed using I$_{2g}$ at the Pickering NGS during 1990 to 1993 are listed in tables 3.8 to 3.11...
The lowest transmission factor was obtained from the PARMS-high-radiation-monitoring sampling system. It was hypothesized the low iodine recovery may have been caused by the small tube inside diameter or the low flow rate or the combination of the two factors.
To test this hypothesis, in the experiment performed on November 30, 1993, the flow rate was increased from 2.5 L/min to 12 L/min, thus increasing the gas linear velocity. The results showed that, initially the iodine recovery was improved to as high as 43%. The recovery, however, continuously declined in the subsequent tests to 4% at the end. No explanation was given for the phenomena. In the next tests series, the inside diameter of the line was increased from 0.457 cm\(^{-1}\) to 0.74 cm\(^{-1}\) by using the PARMS auxiliary sampling lines. The surface to volume ratio was decreased by 39%. During this tests, the air flow rate was kept at a low value of 2.5 L/min. The outcome did not show any improvement. The iodine recovery remained below 2%. Similar tests results were also obtained from Bruce NGS exhaust stack monitoring as well as PARMS systems.

3.9 Summary

Based on the available literature, it is clear that there is a relationship between the amount of iodine retention on stainless steel sampling lines and the operating parameters which include tube inside diameter, length of the sampling line, the number of bends and fittings in the system, the gas flow rate, temperature, relative humidity and iodine gas phase concentration.

Theoretically, iodine transmission fraction could be estimated by using correction factors based on these parameters along with the available empirical data. Despite the large body of data, there are still difficulties in applying the experimental results to a full scale system with confidence. The main problem is that the underlying phenomena which is responsible for iodine retention is still not very well understood.
According to the data presented, any surface reactions that may occur could in fact play a very important role in determining the rate and extent of iodine retention. Two variables that can be identified as very important in determining the surface reactions are temperature and relative humidity. This raises the question as to whether gas phase mass transfer or surface reactions will have the most dominant effect on the rate and extent of iodine retention. For this reason, the current research effort was also directed toward answering this question.

Deposition velocity has been used extensively to describe the iodine retention rate. It is important to point out that deposition velocity may change with time. Deposition velocity may decrease as iodine deposition proceeds, due to depletion of the adsorption sites or the inhibition of any surface reactions. Furthermore, it is possible that deposition velocity is a function of iodine gas phase concentration. The gas phase iodine concentration may also vary with time during an accident. This adds to the already complex situation since gas phase concentration is the variable to be measured.

In the existing literature, there is inadequate data to resolve the difference, if any, between the iodine retention behavior of SS-304L and SS-316L. Despite the expectation that SS-316L should perform better, there appears to be no difference between the two types of steel. In fact, some results suggest that SS-304 will perform better than SS-316L. Therefore, in addition to investigating the effects of operating conditions such as temperature and relative humidity, the purpose of the current research was also to study the differences between SS-304L and SS-316L at various temperatures, relative humidities and iodine gas phase concentrations. It was hoped that the results would lead to a better understanding of the underlying mechanisms that are responsible for iodine retention on stainless steel sampling lines.
4. Experimental

The technique to determine the concentration of iodine deposited on the steel surface relied on the labeling of stable iodine with radioactive $^{131}$I. $^{131}$I was chosen due to its relatively short half life of 8.040 days [34]. The method allowed the detection of iodine surface concentration as low as $10^{-11}$ mol/cm$^2$ which is less than one hundredth of a monolayer. The detection limit depended on the specific activity of radioiodine being used in the experiment which describes the ratio of radioactive $^{131}$I to stable iodine. Typically the specific activity used was between $10^8$ to $10^{11}$ Bq/mol.

A similar technique was used to determine gas phase concentration. This measurement was performed by passing the air stream through TEDA impregnated charcoal filters contained within 0.64 cm (1/4") tygon tubing. The charcoal filters were subsequently counted on an LKB gamma counter containing a 3x3 well type sodium iodide detector. The detector has an efficiency of 55% for the 365.4 keV gamma ray emitted by $^{131}$I. By using the known specific activity, the gas phase iodine concentration was calculated.

4.1 Experimental Apparatus

The arrangement of the apparatus is shown in figure 4.1. The apparatus as well as the methodology was originally designed by Christopher Deir at the University of Toronto [7]. Some modifications were made to it for the current research effort.
As the apparatus allowed concurrent tests of two steel specimens, duplicate in measurement was obtained in every experiment. In spite of this, in some cases it was necessary to repeat an experiment to confirm the trend that was obtained. One of the main difficulties in the design of the equipment was the fact that iodine is very reactive. Iodine would deposit on most materials. To prevent excessive loss of iodine, teflon was chosen as the main material for part of the apparatus in contact with iodine.

The amount of iodine retained within the steel tubing was determined using two 2x2 sodium iodide scintillation detectors. The signal from the detectors was sent to a 386 IBM compatible personal computer equipped with two APTEC MultiChannel Analyzers (MCArds)
each having a 1024 channel capability. An APTEC detection program called Supervisor was used to collect the data. The program was set to collect a measurement every 150 to 600 s depending on the expected rate of retention. For a very slow process, such as desorption, a 600 s counting time was more suitable while for adsorption a 150 to 300 s counting time was used.

4.1.1 General Features

The system allowed the independent control of relative humidity, temperature of the steel specimens, gas flow rate as well as the gas phase iodine concentrations. The system also allowed two steel specimens to be tested concurrently. This was important in obtaining reliable data since the results from the two specimens could be used to verify one another.

The gas stream entering the system was split into three streams with independent flow control systems. A small proportion of the gas stream was diverted to pick up molecular iodine. A bubbler was placed prior to the iodine generator vessel. The purpose was to prevent the depletion of water inside this vessel. More stable concentrations of iodine could be obtained this way.

The relative humidity of the gas could be set from near 0% to as high as 100%. Low range humidity was achieved by using an air dehumidifier system which was placed at the inlet before the air stream was split. The dehumidification unit, which is not shown in the diagram, consisted of drierite to absorb the moisture and molecular sieve to prevent any particulates from entering the system. A higher level of relative humidity could be achieved by increasing the flow that passed through bubbler-1. Any intermediate relative humidity
could be obtained by altering the ratio of the gas flow that passed through the bubbler to the one that bypassed it. This stream then passed through a temperature and relative humidity probe and finally was mixed with the stream that carried the iodine. As mentioned previously, only a small proportion of the gas stream was diverted to the iodine generator vessel. This stream, however, would always contain some humidity. This made it impossible in practice to reach a relative humidity of 0%.

4.1.2 Measurement of Gas Temperature and Relative Humidity

For the purpose of measuring gas temperature and relative humidity, two probes were incorporated into the system. Initially only one probe was used. The first probe was placed prior to the mixing point between the main gas stream and the stream that carried the iodine. This probe was never contaminated with radioiodine. During the later stages of the study, a second probe was installed. This probe was placed after the steel specimens. The purpose was to verify the readings of the first probe and to confirm that there was no significant change in the gas temperature and humidity during transport to the steel specimens. The second probe also allowed the impact of the iodine generator on relative humidity to be determined. This was especially important for experiments under low humidity conditions. Monitoring of the gas phase temperature was very crucial since in some experiments the stainless steel specimens were kept at a temperature as high as 90°C. Due to the very short residence time of the gas within the tube, only slight increases of up to 2°C were observed.
4.1.3 Temperature Control of the Steel Tubing

One of the main variables being investigated was the temperature of the steel tubing. Heating of the steel specimens was carried out by placing the steel sample inside glass tubing which was heated using heating tapes. The control of the temperature was achieved by attaching thermocouples on the outside surface of the steel samples. The temperature read by the thermocouples were fed into PID temperature control systems which were used to manipulate the power output of the heating tapes. The method allowed the temperature of the tubings to be maintained to within ±3°C of the set point.

In the beginning of the study, it was noticed that there was an axial temperature gradient within the tube. This occurred due to cooling at both ends of the steel samples. To reduce this temperature gradient, modifications were made to the way in which the heating tapes were wrapped around the glass tube: heating was slightly more concentrated at both ends of the tubes. A smaller temperature gradient was obtained after this modification was applied. However, despite this modification, a temperature difference of up to 3°C was still observed especially during experiments at high temperature. To monitor the temperature distribution, two more thermocouples were installed on each sample, one at the inlet and the other at the outlet.

4.2 Gaseous I₂ Generation

In this experiment, molecular iodine was generated by using a triiodide method. The process was achieved through reaction 2.5 below.
\[ I_{2(aq)} + I_{(aq)} \leftrightarrow I_{3}^{- (aq)} \]  \hspace{1cm} (R 2.5)

The forward and reverse rate constants of this reaction are \(10^{-10} \text{ M}^{-1}\cdot\text{s}^{-1}\) and \(1.33\times10^{-7} \text{ M}^{-1}\cdot\text{s}^{-1}\) respectively [7]. As \(I_2\) left the solution to the gas phase, it would be immediately replaced by the dissociation of \(I_3^-\). By using this method it was possible to obtain a relatively stable gas phase iodine concentration in the range from \(10^{-7}\) to \(10^{-11}\) mol/L.

The solution was prepared by adding sublimed iodine crystals to a NaI solution. To this solution a sufficient amount of radioiodine tracer was then added. The amount of \(^{131}\text{I}\) required depended on the specific activity required during any particular experiment. Experiments at 90°C and low humidity, for example, required a higher specific activity as compared to experiments at 40°C and high humidity.

### 4.3 The Stainless Steel Samples

Two types of steel tubing were being examined. SS-316L and SS-304L. The specifications of the steel specimens are given in the following table.

Table 4.1 Steel sample specifications

<table>
<thead>
<tr>
<th>Type</th>
<th>Outside Diameter</th>
<th>Wall Thickness</th>
<th>Inside Diameter</th>
<th>Length</th>
<th>Pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-316L</td>
<td>0.64 cm</td>
<td>0.081 cm</td>
<td>0.472 cm</td>
<td>25.4 cm</td>
<td>air blowing</td>
</tr>
<tr>
<td>SS-304L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No specific pretreatment was applied to the steel samples other than smoothing the ends of the tubing sections and blowing air through the tubing to remove any dust particles or steel fragments left during cutting of the tubing. The air blowing was performed for
approximately one half hour. Before an experiment was started the inside of the tubing was inspected visually to make sure that there was no obstruction present.

In the beginning of the study, the length of the steel samples was 6" (15.24 cm). It was found that iodine retention at regions around the inlet and outlet was significantly higher than the average retention in the middle part of the tubings. It was believed that the higher iodine retention was due to turbulence at the inlet region or damage of the oxide layer that made the steel surface more prone to iodine chemical attack. To reduce the impact of this iodine distribution, the length of the tubing samples was increased as much as possible given the space constrain within the fume hood. A 25.4 cm length was chosen. As a result of increasing the tubing length and collimating the gamma detectors using lead, only iodine deposition on the central 18 cm was monitored for radioiodine activity. This was the only part of the samples that could be detected by the sodium iodide detectors. Subsequent tests revealed a flat iodine distribution within this region. In addition, any iodine that was retained by the teflon fittings connecting the steel samples was also not detected.

Some tests were also performed on glass tubing with similar dimensions as the stainless steel samples. Glass is considerably more inert compared to stainless steel in regards to \( I_2 \) deposition. Hence, it was expected that iodine deposition on glass surface would be much lower. The purpose of such tests was to confirm that the measured iodine deposition was due to iodine interaction with the steel surface rather than to any other phenomena such as deposition on the teflon fittings.

In addition to the tests performed on stainless steel tubing, some experiments were also carried out on stainless steel compression fittings. The purpose of these experiments was
to study iodine deposition in the region near the fittings. These experiments were motivated by the concern that fittings might contribute substantially to the total loss of iodine along the sampling lines. The experiments were performed by inserting a stainless steel fitting at the middle part of the steel samples. The activity of radioiodine along the tubing including the stainless steel fitting was monitored throughout the experiment.

4.4 Experimental Parameters

Table 4.2 below shows the experimental conditions that were used in this study. The temperatures given are those of the steel surface while the relative humidities are the ones associated with the gas stream.

Table 4.2 Experimental parameters

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Relative Humidity</th>
<th>Iodine Gas Phase Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>23, 40, 60, 90</td>
<td>Low: 0% &lt; RH &lt; 25%</td>
<td>High: $5 \times 10^{-7} \text{ M} &lt; [I_2]_g &lt; 5 \times 10^{-8} \text{ M}$</td>
</tr>
<tr>
<td></td>
<td>High: 75% &lt; RH &lt; 100%</td>
<td>Med.: $5 \times 10^{-9} \text{ M} &lt; [I_2]_g &lt; 1 \times 10^{-8} \text{ M}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low: $5 \times 10^{-11} \text{ M} &lt; [I_2]_g &lt; 1 \times 10^{-9} \text{ M}$</td>
</tr>
</tbody>
</table>

Tests were performed for every possible combinations of the above experimental settings. The classification of the iodine gas concentration into low, medium and high was arbitrary. As discussed in the literature survey, research into the effect of iodine gas phase concentration on the rate and extent of iodine retention has been scarce.

4.5 Experimental Procedure
To some extent the experimental procedure that was used in the investigation has been mentioned in the preceding sections. The following description is given to compliment the earlier sections, by clarifying a few points and describing others that have not been discussed previously.

Steel tubing sections that had been previously prepared for the experiment were inserted into the detection stations. The tubes were connected by using teflon fittings at both ends. The fittings were then hand tightened. The tubes were carefully placed into the detection systems so that a similar geometry was maintained in each experiment. This was crucial to ensure that the detectors collected gamma events that originated only from the relevant area of the tubing. As it was explained in section 4.3, although the length of the tubing was 25.4 cm, the area that was monitored for iodine deposition was only the central 18 cm"). Upon proper installation of the tube samples, the detectors were put in place above the samples. The temperature controller was then set to bring the samples to the set point temperature. Approximately one hour was required to allow the set point to be reached and stabilized.

Once the temperature stabilized, the Supervisor program was set to collect and save the data every 150 to 600 s. Before an experiment began, the region of interest of the gamma detection system was calibrated. This calibration was necessary since some drifting of the region of interest had been observed in several early experiments, especially in experiments at higher temperatures. The temperature changes between the experiments caused the drifting problems to deteriorate making the calibration procedure a necessary part of the experiment.

The calibration was performed using a short section of glass tubing that contained some charcoal which was loaded with $^{131}$I. Three main gamma lines of $^{131}$I were used in the
calibration process, i.e. at 284.3 keV, 364.5 keV and 637 keV. The region of interest was then set to collect data corresponding to the iodine peak at 364.5 keV which is the most dominant gamma emission associated with the decay of $^{131}$I.

After the calibration procedure was completed, the vacuum pump was turned on. The gas flow was adjusted to the set value of flow rate and relative humidity. The temperature of the gas stream was ambient in all the experiments. The flow rate used in this study was 1.5 L min. Before an experiment was started, the gas concentration was checked to ensure that the value was within the intended range.

The gas sampling process was carried out by inserting a short section of tygon tubing containing TEDA impregnated charcoal filter into the gas sampling port. The gas flow was allowed to pass through the filter for a period of 30 seconds to 2 minutes. Longer times were required to obtain an iodine activity that was well above the background value. The charcoal filter was then counted in the LKB Compugamma system. Combining the information on the specific activity, the iodine activity collected in the filter and the total volume of gas that passed through the tubing, the iodine gas phase concentration could then be calculated.

Once all of the initiation procedure was completed, the Supervisor program was set to commence the data collection. During the first hour, background radiation was evaluated. Throughout this period, the gas stream was allowed to flow in the by-pass mode. At the end of this first hour, the by-pass line was closed. The gas began to pass through the steel specimens. At this point the first gas sample was taken. Subsequent sampling of the gas was carried out at intervals of one hour to 1.5 hours. Most experiment lasted for about four hours. Some experiments had to be terminated before four hours had elapsed to prevent accumulation of
too high a radioiodine activity on the tubing. This was for safety reasons as the tubing had to be cut at the end of the experiment in order to evaluate the efficiency of the detectors.

When the temperature of the steel samples had sufficiently cooled, the steel samples were removed from the apparatus. The tubing was cut into 3 cm sections, with the exception of the inlet part which was 5 cm and the outlet section which was 2.4 cm. The tubing sections were subsequently counted in the LKB Compugamma. By comparing the gamma activity measured using the LKB with the final counts from the on-line detectors, the efficiency of the on-line detection system was calculated. In most experiments, the efficiency of the gamma line at 364.5 keV ranged between 1% to 1.8%. This average value of efficiency accounted for the variation at points along the steel tubings due to differing distances from the detectors.

In some experiments, desorption of iodine from the tube surface was carried out. Desorption is a much slower process compared to deposition. The length of the experiment might last between 24 hours to three days. Due to time constraints, desorption was not performed at the end of every experiment. Furthermore, for some conditions such as at high temperatures, low humidity and low gas phase concentration, very low iodine retention was observed. Desorption at the end of these experiments would have lowered the amount of iodine on the tube surface making it impossible to accurately determine the efficiency of the detectors at the end of the experiment.
4.6 UV Spectrophotometry

To complement the results obtained from the procedure involving radioiodine, some experiments utilizing spectrophotometry were also performed. The purpose of these experiments was to identify any products of the reactions occurring on the steel surface such as Fe$^{2+}$ and Fe$^{3+}$. The method was based on the technique developed by Harvey et al. which involved the addition of 1.10 phenantroline to an aqueous solution containing the Fe$^{2+}$ and Fe$^{3+}$ ions [35]. This procedure allowed the concentration of Fe$^{2+}$ and the total concentration of Fe to be determined.

In order to perform the above analysis, a solution containing the reaction products from the inside surface of the steel tubings was required. Steel samples were exposed to a gas stream containing iodine for 4 hours at ambient temperature. The inside of the tubing was then rinsed with 5% HNO$_3$ solution for approximately 10 minutes. The solution was analyzed using Varian Cary 3 UV-VIS spectrophotometer.

In addition to this, some experiments were also carried to investigate the volatilization of iodine from FeI$_2$ solution. This experiment was performed toward the end of the projects. It was performed to confirm the observation that I$_2$(g) was produced from a saturated solution of FeI$_2$. The analysis was based on the reaction of I$_2$ with I$^-$ producing I$_3^-$. The concentration of I$_3^-$ was examined using its absorption at 350 nm. This method had been demonstrated by Palmer et al. [36] and was later used by Tsukaue et al. [8,9]. Palmer et al. reported a value of
25.750 L mol.cm$^{-1}$ for the molar absorptivity of $I_3^-$ at 350 nm. This experiment along with the results are discussed in more detail in section 5.4.3.
5. RESULTS AND DISCUSSION

In this chapter, the results of the experiment are discussed\(^1\). In section 5.1 the variables defining the experimental conditions studied are classified. In section 5.2, the main deposition parameters used to described the results, the deposition velocity \((k_d)\) and maximum surface loading \((C_v^\text{m})\), are discussed. In section 5.3, the impact of the operating conditions on these deposition parameters is described. Various experiments performed to evaluate desorption are presented in section 5.4.

In section 5.5, a mechanistic interpretation of the overall adsorption and desorption trends is presented and evaluated in terms of the experimental results. It is proposed that \(I_2\) is deposited through three distinct mechanisms. Physical adsorption alone occurs when gas phase concentration is below \(10^{-9}\) mol/L. A second mechanism occurs for gas concentration above \(10^{-9}\) mol/L when little water is present on the steel surface, for example at low relative humidity or high temperature. When adequate water is on the surface, a corrosion type chemisorption mechanism predominates. Here, \(I_2\) is believed to react at defect sites on the surface to form hygroscopic \(\text{FeI}_2\) which attracts more water propagating the corrosion. Under some conditions, the propagation is inhibited while for other conditions, no such inhibition occurs resulting in extensive and very rapid iodine adsorption. In section 5.6, the relevance of the results of this study to losses in sample lines is evaluated.

\(^1\) Only selected experiments and compilations of the results are presented in this chapter. The detailed results of every experiment are presented in appendix A and B.
5.1 Variables Studied

In studying the effects of various operating conditions on iodine deposition, every possible combination of the variables chosen was attempted. The range of these variables are described in Table 5.1 below. During the experiments, the values were set at certain ranges as allowed by the experimental apparatus.

**Table 5.1 Range of Variables Investigated**

<table>
<thead>
<tr>
<th>Gas Phase Concentration (Mol/L)</th>
<th>Tube Surface Temperature (°C)</th>
<th>Relative Humidity (*)</th>
<th>Steel Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low: $10^{-11}$ to $10^{-5}$</td>
<td>23°C, 40°C. 60°C, 90°C</td>
<td>Low: 0% to 25%</td>
<td>SS-316L and SS-304L</td>
</tr>
<tr>
<td>Medium: $10^{-2}$ to $5\times10^{-8}$</td>
<td>High: 75% to 100%</td>
<td></td>
<td>Size: 0.47 cm ID. and 0.64 cm OD.</td>
</tr>
<tr>
<td>High: $5\times10^{-8}$ to $5\times10^{-7}$</td>
<td>(*) Several experiments were also performed at medium relative humidity ranging between 45% to 55%.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The range of values described in Table 5.1 was designed so that the set points could be attained despite any fluctuations that might occur during the experiment. Furthermore, the conditions investigated were selected in order to provide an adequate representation of the operating conditions that might arise in actual gas sampling systems, both during testings and a reactor accident. The basis for the classification used in Table 5.1 is discussed in Appendix D along with some of the limitations in controlling the variables and the overall experimental reproducibility.
5.2 Deposition Parameters

Before discussing the effects of the operating conditions on iodine deposition behavior, it is important to first describe the two parameters selected to represent the trends. Specifically, most of the results can be described in terms of the initial deposition velocity \((k_d)\) and the maximum surface loading \((C_v^0)\). Under many conditions, desorption did not contribute significantly to the observed behavior. Desorption is described in section 5.4.

5.2.1 The Deposition Velocity \((k_d)\)

The most common parameter used to describe the rate of \(I_2\) retention is the deposition velocity \((k_d)\) which represents the \(I_2\) deposition rate normalized by the gas phase concentration. This parameter is regarded as convenient to use since it can be applied to any system without considering the amount of \(I_2\) contained in the gas stream. In practice, this is especially useful if \(I_{2(g)}\) concentration is the variable being measured. Furthermore, \(k_d\) is also practical in the identification of the rate determining step in the deposition process as the value can be directly compared with the theoretical gas phase mass transfer coefficient, \(k_g\). This is of significant importance since once the limiting step is identified, any effort to limit iodine losses can be focused on manipulating the factors that affect this rate determining step. The following figure shows the variation of \(k_d\) as a function of \(I_2\) gas phase concentration for SS-316L.
Figure 5.1 Variation of $k_d$ with gas phase concentration for SS-316L.

As can be seen in figure 5.1 the $k_d$ values appear to be divided into two groups in terms of the relative humidity. At high relative humidities, at gas concentration above $10^{-6}$ mol/L, $k_d$ is relatively constant with a value on the order of 0.1 cm/s. This lack of dependence of $k_d$ on concentration gives support to the assumption underlying the use of $k_d$, that deposition rate is a first order function of gas concentration. At low relative humidities, $k_d$ decreases with increasing concentration indicating that the deposition rate is only a weak function of the gas concentration. This trend is not consistent with the first order assumption implicit in the definition of $k_d$. This type of behavior has never before been identified in relation to the deposition of $I_2$ on steel. A more detailed discussion concerning the variation of $k_d$ under different operating conditions can be found in section 5.3 while speculation regarding the underlying mechanisms is presented in section 5.6.

From the results of this research, there is evidence that the use of $k_d$ alone may not adequately represent deposition trends. A second important assumption in the use of $k_d$ alone is that $I_2$ loading increases linearly with time. This assumption, in most cases, can only be applied
during the early stage of deposition. Beyond this initial period, the deposition rate will often decline until eventually a maximum loading is achieved. Thus, beyond the initial stage of deposition, the assumption of linear accumulation no longer holds. An example of such results can be seen in figure 5.2 below. A declining deposition rate was observed under most experimental conditions.

![Graph showing temporal variation of iodine surface loading](image)

**Figure 5.2 Temporal variation of iodine surface loading**

Based on these considerations, caution should be taken in using \( k_d \) as the only parameter. Although \( k_d \) contains information on how fast \( I_2 \) will initially deposit on the tube surface, it does not always describe how deposition will behave over extended periods of time. Because \( k_d \) does not contain information on the extent of iodine deposition, it does not predict the occurrence of maximum loading on the steel surface. Thus, the use of \( k_d \) has to be accompanied by the knowledge on how iodine deposition is changing with time.

This problem has typically not been identified as crucial mainly due to the methodology used previously in studying \( I_2(g) \) deposition. In the literature, the reported values of \( k_d \) are commonly based solely on the amount of \( I_2 \) accumulated on the tube surface at the end of an
experiment, or on the fraction of the iodine transmitted through a length of tubing i.e. the
transmission fraction. Hence, the actual accumulation of I₂ on the surface as a function of time is
absent. For such experiments, a constant deposition rate is implicitly assumed. The values of
deposition velocity used in this report are only relevant to the initial stage of deposition during
which a constant deposition rate was observed.

5.2.2 Pseudo-saturation Surface Concentration (Cₚ₀)

As mentioned previously, the use of kₚ alone which implies iodine accumulation at a
constant rate, does not predict the existence of any maximum surface loading. Therefore another
parameter must be used to represent the maximum loading. The combination of the two
parameters better represents the phenomena of iodine deposition. Figure 5.3 shows the variation
of maximum iodine loading as a function of gas phase concentration. The values include data for
SS-316L and SS-304L at all the temperatures and humidities examined.

![Diagram of Maximum Iodine Surface Loading vs [I₂]g](image)

Figure 5.3 Maximum iodine surface loading as a function of gas phase concentration

As shown above, the point where the system reached maximum loading varied depending
on the relevant operating conditions. As there was no single value of saturation concentration, the
term pseudo-saturation concentration, denoted by $C_s'$. is used to represent this apparent maximum loading. It is important to note that figure 5.3 only reflects some of the experimental results. For examples, experiments at high and medium concentration, under high relative humidity with tube temperatures of 40°C and 60°C, did not show any maximum loading: $I_2$ loading continued to climb despite the high surface concentration already achieved ($<10^{-7}$ mol/cm$^2$). Furthermore, some experiments, particularly those under low gas phase concentrations that resulted in very low iodine loading rates are not included in figure 5.3. It would have taken a long time for the system to reach maximum loading, hence, many of these experiments were terminated before the plateau region was achieved. Furthermore, in some other experiments, the value was below the detection limit, therefore they are not reflected in figure 5.3.

5.2.3 Steady state and Surface Pseudo-saturation

Maximum surface loading may occur due to two possible phenomena. The first one is the steady state condition. Steady state occurs when the rate of adsorption is equal to the rate of desorption preventing any further $I_2$ accumulation on the steel surface. This phenomena can be identified by the high rate of desorption. Furthermore, it also suggests that physical adsorption is responsible for the deposition process. Mathematically, the balance between the two rates, described in chapter 2, is given by equation 2.3.

$$\frac{dC_s'}{dt} = k_d C_g' - k C_s' \quad (2.3)$$

Another possibility is that surface saturation was achieved during the experiment. If such saturation occurred, $k_d$ would be effectively zero. Consequently, equation 2.3 above would no
longer be valid. A different basic equation to describe iodine deposition would have to be used. This equation must take into account the possibility of maximum surface loading due to saturation. An equation which can be used to derive the Langmuir isotherm is used in this report. The equation requires the use of an additional parameters that represents surface saturation.

\[ \frac{dC_s}{dt} = k_d(1 - \frac{C_s}{C_s^*})C_s - kC_s \]  

(eqn. 5.1)

The ratio of \( C_s/C_s^* \) can be explained as the term that describes the distance between iodine surface concentration at any point of time to the surface concentration at saturation. In effect, this term will bring the curve of iodine surface concentration to asymptotically approach the saturation value. As equation 5.1 also includes a desorption term, it also represents the role of desorption in determining the value of maximum surface loading.

In the discussion to follow (section 5.4), it will be shown that, particularly under high relative humidity conditions, the maximum loadings under some conditions are more consistent with surface saturation than a steady state.

5.3 The Effects of Operating Conditions on Deposition Parameters

Throughout the project, the rate and extent of deposition was observed to vary with the operating conditions. In this section, the effects of the operating conditions on the two main deposition parameters, \( k_d \) and \( C_s^* \), are discussed. A number of relationships between these parameters and the operating conditions are identified. The discussion begins by considering the effect of gas phase concentration. Based on this division, the effect of tube surface temperature
and relative humidity are also considered. The data from SS-316L and SS-304L are presented together so that comparison can be readily made.

5.3.1 High Iodine Concentration

Compared to the two other concentration ranges, the results for high concentration showed the clearest trend. The observed values of $k_d$ for high gas phase concentration are shown in figures 5.4.

![Figure 5.4a and 5.4b Deposition Velocity at High $[I_2]$](image)

Both figures illustrate the substantial effect of humidity on $k_d$. The impact was particularly pronounced at 40°C and 60°C but less significant at 23°C and 90°C. At 90°C, the rate of deposition appeared to be suppressed. In fact, at 90°C, for both SS-316L and SS-304L, there was little or no difference in the rate of deposition at high and low relative humidity.

The highest iodine loadings were observed with high relative humidity and tube temperatures of 40°C or 60°C. Under these conditions, iodine deposition continued to climb with a high deposition velocity on the order of $10^{-1}$ cm/s and no evidence of pseudo-saturation of the surface was observed (figure 5.5). It was observed that under these operating conditions, there was an initial delay period after which iodine accumulated at a constant and very rapid rate.
When this type of behavior was observed, for a more accurate representation of the deposition rate, $k_d$ associated with the linear part during which the highest deposition rate occurred was reported.

![Graph](image)

Figure 5.5 Iodine surface loading at 40°C, high gas phase concentration and high relative humidity

A high deposition rate was also observed for SS-316L at 23°C and low relative humidity (figure 5.6). This was somewhat unexpected. The surface concentration actually surpassed the maximum loading at high relative humidity which was on the order of $10^{-7}$ mol/cm$^2$. When relative humidity was increased to near 100%, rapid iodine desorption occurred. The surface concentration which initially exceeded $10^{-6}$ mol/cm$^2$ was decreased to approximately $9 \times 10^{-7}$ mol/cm$^2$ and was still decreasing slowly when the experiment was terminated. It is not clear why such behavior would occur. Similar deposition behavior was not observed for SS-304L. Under the same operating conditions, the value of $k_d$ was much lower. It is not clear as to what caused the differences.

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It should noted that this experiment was performed using tubing obtained from the same supplier as that used by Deir [7,17]. In all the other experiments performed in the present study, the tubing was purchased from an alternate source.
Figure 5.6 Iodine surface concentration high [I$_2$]g and low relative humidity

The amount of data on maximum surface loading ($C_s^a$) is very limited. As a result, it is difficult to justify any definite dependence of $C_s^a$ on temperature or relative humidity. In spite of this, figure 5.3 suggests that a combination of high tube temperature and low relative humidity decreases the maximum loading. For example, at 23°C and high humidity, $C_s^a$ was $10^{-7}$ mol/cm$^2$. When the temperature was increased to 90°C, $C_s^a$ was reduced to $10^{-8}$ mol/cm$^2$. At tube temperature of 90°C but low relative humidity, $C_s^a$ was further suppressed to $10^{-9}$ mol/cm$^2$. A similar trend was observed at 40°C. Under high relative humidity, at the end of the experiment, the surface concentration was higher than $2 \times 10^{-7}$ mol/cm$^2$ and was still increasing. At low relative humidity, however, $C_s^a$ was reduced to $5 \times 10^{-9}$ mol/cm$^2$. The above observation, again, confirmed the role of water in enhancing the rate and extent of iodine deposition on stainless steel. A closer analysis of figure 5.3 shows that the impact of gas phase concentration on $C_s^a$ was more significant than the impact of both relative humidity and tube temperature. Under high gas phase concentration, the impact of relative humidity is still clearly visible. When gas phase concentration was reduced to below $10^{-9}$ mol/L, however, $C_s^a$ seemed to be unaffected by the differences in gas relative humidity.
The above observation on the variation of both \( k_d \) and \( C_i^0 \) with temperature and relative humidity suggests that any chemical interactions on the surface that can enhance iodine deposition require the presence of water. The amount of water on the surface may be affected by a combination of tube surface temperature and relative humidity. Higher temperature should decrease the amount of surface water but may increase the rate of chemical reactions. Higher humidity should increase the amount of water on the steel surface. Deir [7] suggested that at high temperature such as 90°C, the amount of water available on the surface is significantly reduced so that any surface reactions which require the presence of water are inhibited. Deir also suggested that a mechanism involving corrosion attack of the steel by iodine which requires surface water is likely.

Furthermore, it can also be seen that at 40°C and 60°C both SS-316L and SS-304L were equally susceptible to high iodine deposition rates especially at high relative humidity. Deir [7] reported that similar behavior was also observed for medium of relative humidity (~50%). At 23°C, SS-304L seemed to perform better than SS-316L. This was true for both ranges of relative humidity. This is consistent with the observation by Lee et al. [26] but is contrary to what was expected. As discussed in chapter 3, the main difference between SS-316L and SS-304L is the addition of molybdenum in SS-316L. Molybdenum is known to increase steel’s resistance to pitting corrosion attack by chlorine.

5.3.2 Medium Gas Phase Concentration

The plot of \( k_d \) as a function of temperature for high and low relative humidity can be seen in the following figures.
Figure 5.7a and 5.7b Deposition velocity at medium concentration

As can be seen above, for SS-316L, $k_d$ was consistently higher at high relative humidity. Scattering occurred at 23°C and high relative humidity. It is not clear why this scattering occurred. Similar to the trend observed at high concentration, a high deposition rate was also observed at high humidity and temperatures of 40°C or 60°C. The values of $k_d$ at low relative humidity were consistently lower. It should be noted that the extent of deposition on SS-316L at 90°C was below detection indicating that the deposition velocity was less than $10^{-3}$ cm/s. The values of the detection limit were used to calculate the $k_d$ values in figure 5.7a for SS-316L at 90°C.

SS-304L showed different trends than SS-316L. At 23°C, $k_d$ was low and there appeared to be no significant effect of relative humidity. The highest value of $k_d$ was observed at 40°C and low relative humidity. This is somewhat perplexing as previously, for high gas phase concentration, the highest $k_d$ was observed at 40°C or 60°C and high relative humidity. At low humidity, however, the accumulation stopped at loadings between $3 \times 10^{-9}$ to $6 \times 10^{-9}$ mol/cm². At high humidity the loadings was $2 \times 10^{-9}$ mol/cm² and was still increasing when the experiment was terminated (table 5.2).
The data from the two types of steel suggest that under high relative humidity with temperature lower than 90°C, at medium gas phase concentration SS-304L performs better than SS-316L. At 90°C, for SS-316L humidity appeared to have no effect on $k_d$. Furthermore, the value was found to be lower than $k_d$ at temperature between 23°C to 60°C. SS-304L, however, showed high $k_d$ at 90°C and high humidity (~10^{-1} cm/s). At low relative humidity, $k_d$ was found to be approximately $10^{-2}$ cm/s.

Under low humidity condition, SS-316L appears to perform better than SS-304L especially at 40°C. An interesting observation is that for SS-316L at low humidity, temperature seems to have no effect on $k_d$. The only difference is in the values of maximum loading (table 5.3). At 60°C, the maximum loading achieved was higher than $10^{-10}$ mol/cm² while at 23°C and 40°C, the loading was between $2x10^{-10}$ to $8x10^{-10}$ mol/cm² and was still increasing when the experiment was terminated.

**Table 5.2 SS-304L Medium \[I_2\]g**

<table>
<thead>
<tr>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High relative humidity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$4.0 \times 10^{-3}$</td>
<td>-40</td>
<td>$5 \times 10^{-2}$</td>
<td>$&gt;2\times 10^{-9}$ mol/cm²</td>
</tr>
<tr>
<td>$4.0 \times 10^{-3}$</td>
<td>-40</td>
<td>$1.7 \times 10^{-2}$</td>
<td>$&gt;2\times 10^{-9}$ mol/cm²</td>
</tr>
<tr>
<td><strong>Low relative humidity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$4.5 \times 10^{-3}$</td>
<td>-40</td>
<td>1.01</td>
<td>$3\times 10^{-9}$ mol/cm²</td>
</tr>
<tr>
<td>$4.5 \times 10^{-3}$</td>
<td>-40</td>
<td>$5.46 \times 10^{-1}$</td>
<td>$6\times 10^{-9}$ mol/cm²</td>
</tr>
<tr>
<td>$1.7 \times 10^{-3}$</td>
<td>-40</td>
<td>$4.6 \times 10^{-1}$</td>
<td>$5\times 10^{-9}$ mol/cm²</td>
</tr>
<tr>
<td>$1.7 \times 10^{-3}$</td>
<td>-40</td>
<td>$3.41 \times 10^{-1}$</td>
<td>$3.5\times 10^{-9}$ mol/cm²</td>
</tr>
</tbody>
</table>
Table 5.3 SS-316L Medium $[I_2]_g$ - Low %RH

<table>
<thead>
<tr>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$kd$ (cm/s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.2 \times 10^{-8}$</td>
<td>23</td>
<td>$4 \times 10^{-3}$</td>
<td>$&gt; 4 \times 10^{-10}$ mol/cm$^2$</td>
</tr>
<tr>
<td>$2.1 \times 10^{-8}$</td>
<td>23</td>
<td>$2.3 \times 10^{-3}$</td>
<td>$&gt; 3 \times 10^{-10}$ mol/cm$^2$</td>
</tr>
<tr>
<td>$3 \times 10^{-8}$</td>
<td>-40</td>
<td>$5 \times 10^{-3}$</td>
<td>$&gt; 8 \times 10^{-11}$ mol/cm$^2$</td>
</tr>
<tr>
<td>$5 \times 10^{-8}$</td>
<td>-40</td>
<td>$2 \times 10^{-3}$</td>
<td>$&gt; 8 \times 10^{-10}$ mol/cm$^2$</td>
</tr>
<tr>
<td>$3 \times 10^{-8}$</td>
<td>-40</td>
<td>$1 \times 10^{-3}$</td>
<td>$&gt; 2 \times 10^{-10}$ mol/cm$^2$</td>
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<tr>
<td>$2 \times 10^{-9}$</td>
<td>60</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-10}$ mol/cm$^2$</td>
</tr>
<tr>
<td>$2 \times 10^{-9}$</td>
<td>60</td>
<td>$2.6 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-10}$ mol/cm$^2$</td>
</tr>
</tbody>
</table>

From figure 5.3, it can also be seen that maximum loading was higher at high than at low relative humidity. This behavior was similar to the one observed under high gas phase concentration. The effect of temperature is much less clear. However, higher temperature appeared to lower maximum iodine loading. This can be seen in both figure 5.3 and table 5.3 above.

5.3.3 Low Iodine Gas Phase Concentration

Figures 5.8a and 5.8b below show the plot of deposition velocity as a function of temperature for both SS-316L and SS-304L. It should be noted that the SS-316L data are mostly based on the detection limit. It can be seen that scattering occurred for SS-316L especially under low relative humidity.
Figure 5.8a and 5.8b Deposition Velocity for SS-316L and SS-304L as a function of Temperature

These results suggest that at low gas phase concentration, tube surface temperature and relative humidity had very little effect on $k_d$. Almost all values fluctuate between $10^{-2}$ to $10^{-1}$ cm/s. At high humidity, SS-316L appeared to perform better than SS-304L. Under low humidity condition, however, the picture is less clear as there is scattering in the data.

Tube surface temperature and relative humidity appeared to have little or no effect on the values of maximum surface loading. All the values are on the order of $10^{-10}$ mol/cm$^2$. The only exception was that at 60°C and 90°C, with humidity in the lower range, surface loading decreased to $10^{-11}$ mol cm$^2$. A summary of results for SS-304L can be found in table 5.4 and 5.5 below.
Table 5.4 SS-304L Low [I\textsubscript{2}]\textsubscript{e} - High %RH

<table>
<thead>
<tr>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>kd (cm/s)</th>
<th>Deposition rate (mol/cm\textsuperscript{2}.s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6 x10\textsuperscript{-11}</td>
<td>23</td>
<td>2 x10\textsuperscript{-1}</td>
<td>1.7 x10\textsuperscript{-14}</td>
<td>1.5 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>7.6 x10\textsuperscript{-10}</td>
<td>23</td>
<td>6 x10\textsuperscript{-2}</td>
<td>4.2 x10\textsuperscript{-14}</td>
<td>2.5 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>2.5 x10\textsuperscript{-11}</td>
<td>40</td>
<td>1.8 x10\textsuperscript{-1}</td>
<td>4.4 x10\textsuperscript{-14}</td>
<td>&gt; 6 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>2.2 x10\textsuperscript{-11}</td>
<td>40</td>
<td>1.1 x10\textsuperscript{-1}</td>
<td>2.5 x10\textsuperscript{-14}</td>
<td>&gt; 3.5 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
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<td>40</td>
<td>1.2 x10\textsuperscript{-1}</td>
<td>2.63 x10\textsuperscript{-14}</td>
<td>&gt; 3.5 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>3.5 x10\textsuperscript{-10}</td>
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<td>9.7 x10\textsuperscript{-14}</td>
<td>3.4 x10\textsuperscript{-14}</td>
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</tr>
<tr>
<td>3.5 x10\textsuperscript{-10}</td>
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<td>4 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>4.3 x10\textsuperscript{-11}</td>
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<td>9 x10\textsuperscript{-2}</td>
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</tr>
<tr>
<td>4.3 x10\textsuperscript{-11}</td>
<td>90</td>
<td>7 x10\textsuperscript{-2}</td>
<td>3.1 x10\textsuperscript{-14}</td>
<td>3 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
</tbody>
</table>

Table 5.5 SS-304L Low [I\textsubscript{2}]\textsubscript{e} - Low %RH

<table>
<thead>
<tr>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>kd (cm/s)</th>
<th>Deposition rate (mol/cm\textsuperscript{2}.s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x10\textsuperscript{-11}</td>
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<td>1.9 x10\textsuperscript{-1}</td>
<td>1.87 x10\textsuperscript{-14}</td>
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</tr>
<tr>
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<td>23</td>
<td>1 x10\textsuperscript{-1}</td>
<td>1.09 x10\textsuperscript{-14}</td>
<td>1.7 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>1.2 x10\textsuperscript{-11}</td>
<td>40</td>
<td>3.9 x10\textsuperscript{-1}</td>
<td>4.7 x10\textsuperscript{-14}</td>
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</tr>
<tr>
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<td>40</td>
<td>3.8 x10\textsuperscript{-1}</td>
<td>4.56 x10\textsuperscript{-14}</td>
<td>&lt; 5 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>5.5 x10\textsuperscript{-10}</td>
<td>40</td>
<td>1.1 x10\textsuperscript{-1}</td>
<td>5.9 x10\textsuperscript{-14}</td>
<td>&lt; 7 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>5.5 x10\textsuperscript{-10}</td>
<td>40</td>
<td>1.3 x10\textsuperscript{-1}</td>
<td>7.3 x10\textsuperscript{-14}</td>
<td>&lt; 9 x10\textsuperscript{-10} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>2.8 x10\textsuperscript{-11}</td>
<td>60</td>
<td>4 x10\textsuperscript{-2}</td>
<td>1 x10\textsuperscript{-14}</td>
<td>1.5 x10\textsuperscript{-11} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>2.8 x10\textsuperscript{-11}</td>
<td>60</td>
<td>6 x10\textsuperscript{-3}</td>
<td>2 x10\textsuperscript{-15}</td>
<td>&lt; 2 x10\textsuperscript{-11} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>6.6 x10\textsuperscript{-11}</td>
<td>90</td>
<td>7 x10\textsuperscript{-3}</td>
<td>4.4 x10\textsuperscript{-14}</td>
<td>4 x10\textsuperscript{-11} mol/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>6.6 x10\textsuperscript{-11}</td>
<td>90</td>
<td>1.6 x10\textsuperscript{-2}</td>
<td>1.1 x10\textsuperscript{-14}</td>
<td>4 x10\textsuperscript{-11} mol/cm\textsuperscript{2}</td>
</tr>
</tbody>
</table>
5.3.4 The overall effects of Gas Phase Concentration

In sections 5.3.1 to 5.3.3, the effect of relative humidity and tube surface temperature are considered for the three ranges of gas phase concentration. This section is focused on presenting the overall picture of the effects of gas phase concentration on the deposition parameters, $k_d$ and $C_{i_2}$. In the beginning of the project, it was thought that the mechanism of iodine deposition might be different at different relative humidity. Figure 5.1 shows the plot of $k_d$ as a function of gas phase concentration. The figure confirms the previous observation of higher $k_d$ at high relative humidity. The effect of temperature, however, is much less clear with the exception of 90°C. At 90°C, relative humidity does not have significant impact on $k_d$ with the value of $k_d$ following the trend of experiments performed under dry condition. At this temperature, the amount of water on the surface was likely suppressed. An interesting observation is that at gas concentration less than $10^{-4}$ mol/L, temperature and relative humidity did not seem to have a significant effect on $k_d$. It is speculated that the mechanism for iodine deposition at concentration less than $10^{-4}$ mol/L is predominantly physical adsorption, in which case relative humidity would not have much impact. At concentration above $10^{-4}$ mol/L, it is speculated that a corrosion type chemisorption mechanism predominated, but only if adequate water was available on the surface. This mechanisms may have been self perpetuating. Specifically, if the chemical interactions between $I_2$ and the steel resulted in a compound that was hygroscopic in nature, the compound would have attracted water from the gas phase thus increasing the amount of surface water. This hygroscopic property may have further sustained the chemical interaction thus increasing the probability of the reactions to propagate. The consequence was the enhancement of rate and extent of iodine deposition.
The dependence of $k_d$ on gas concentration for SS-304L is less clear than for SS-316L (figures 5.1 and 5.9). At gas concentration higher than $10^{-9}$ mol/L, the dependence of $k_d$ on relative humidity is surprising, in that for some gas concentrations the $k_d$ values for dry and humid conditions appear to be reversed. However, at gas concentrations lower than $10^{-9}$ mol L, the trend is similar to that for SS-316L and $k_d$ did not appear to be affected by relative humidity or temperature.

The observation based on the value of maximum surface loading reveals the same significance of gas phase concentration of $10^{-9}$ mol/L. In figure 5.3, it can be seen that above $10^{-9}$ mol L, $C_s^0$ is higher under humid conditions while at gas concentration below $10^{-9}$ mol/L, the values of $C_s^0$ do not seem to be affected by relative humidity or temperature. Furthermore, results under high humidity showed a sudden decrease in $C_s^0$ from $10^{-7}$ mol/cm$^2$ to $10^{-10}$ mol/cm$^2$ when gas phase concentration was lowered to below $10^{-9}$ mol/L.

An additional observation can be made in regard to the values of $C_s^0$. At low relative humidity, the effect of changing gas concentration was more dominant than the impact of tube surface temperature (figure 5.3). Furthermore, the slope of the plot was approximately one
suggesting a constant ratio between the surface loading and the gas concentration. Calculation of the distribution coefficient \(K_D\), the ratio of surface loading to gas concentration, demonstrated that this ratio was in fact independent of gas concentration under these conditions (figure 5.10).

![Distribution Coefficient (K_d) Vs Gas Concentration](image)

**Figure 5.10** Variation of distribution coefficient with gas concentration at low relative humidity

From figure 5.10, it can be seen that under low relative, the values of \(K_D\) is approximately 1000 cm as long as the gas concentration remains below \(10^{-8}\) mol/L. It is possible that under this range of gas phase concentration, iodine concentration on the surface was determined by an equilibrium with the gas phase concentration. Furthermore, this suggests that physical adsorption was the predominant type of adsorption. As a point of comparison, figure 5.11 below summarizes the values of \(K_D\) for results under high relative humidity. It can be seen that the trend is quite different. It is interesting that when gas concentration is below \(10^{-9}\) mol/L, the values of \(K_D\) for high gas phase concentration at high relative humidity is similar to that observed for low relative humidity. This further supports the previous conclusion that below \(10^{-9}\) mol/L, the mechanism of deposition is similar regardless of the relative humidity with physical adsorption likely being the most dominant form of interaction.
5.3.5 Summary of the Effects of Operating Conditions on $k_d$ and $C_s''$

Generally, both $k_d$ and $C_s''$ are higher at high relative humidity. The highest rate and extent of deposition can be expected at 40°C or 60°C under high humidity. This is true for both SS-316L and SS-304L. At these conditions, both types of steel appear to be equally susceptible to chemical attack by iodine. Specifically in terms of $C_s''$, temperature seemed to have less impact than gas phase concentration.

When gas phase concentration was higher than $10^{-9}$ mol/L, the deposition rate depended strongly on relative humidity. Below $10^{-9}$ mol/L, however, a different picture emerged. At this range of concentration, the impact of relative humidity and temperature on $C_s''$ was small as compared to the effect of gas concentration. It is likely that at concentration below $10^{-9}$ mol/L, single mechanism is behind the deposition. One possible interpretation, which is elaborated in section 5.6, is that, at low iodine loadings, insufficient amounts of hygroscopic FeI$_2$ is present on the surface to enhance the accumulation of water by the surface.
In many instances SS-304L appears to perform better than SS-316L. This is somewhat contrary to what is predicted. SS-316L is expected to perform better due to its high content of the element molybdenum which is generally known to protect the steel from pitting corrosion attack by chlorine. The results at low gas phase concentration are not conclusive as practically all results fell below detection limit. During these experiments, however, similar radioiodine specific activity was used which implies that at low gas concentration, SS-316L may perform better than SS-304L.

5.4 Desorption

Despite the fact that the data obtained on the rate of desorption was limited, it did provide some useful insight, especially on addressing the question as to whether the maximum surface loading was due to surface saturation or steady state. Specifically at steady state, the rates of iodine deposition and desorption should be equal. Hence it was possible to calculate desorption rate constants from the observed maximum loadings and deposition velocities using equation 2.3. If, for a given experiment, the maximum loading was actually a steady state, the calculated desorption rate constant would have been similar to the value observed experimentally. The data obtained on desorption is summarized in appendix C.

As an example, data from an experiment with SS-304L under dry conditions, at 90°C and high gas concentration was examined. The value of $k_d$ associated with the experiment was 0.026 cm's and a maximum surface loading of $1.8 \times 10^{-9}$ mol/cm$^2$ was achieved, based on the assumption of steady state, the calculated value of the desorption constant was $1.3 \times 10^{-3}$ s$^{-1}$. However, the experimental data indicated a much lower desorption rate constant of $4.6 \times 10^{-5}$ s$^{-1}$. 
This large discrepancy between the desorption constant predicted by equation 2.3 and the experimental value indicated that the maximum loading was not due to a steady state having been achieved. Figure 5.12 was obtained by calculating iodine surface concentration based on equation 2.3 and equation 5.1. However, for equation 5.1, the experimental value of the desorption rate constant was used in the calculation.

![I₂ Surface Concentration Vs Time](image)

**Figure 5.12** Surface loading as a function of time: experimental and calculated ($[I₂]_c = 8 \times 10^{-8}$ mol/L. $T=90^\circ$C. high relative humidity).

Both equations were capable of predicting iodine loading as a function of time within reasonable performance. However, equation 2.3 which is based on the assumption of steady state over predicted the rate of desorption. On the other hand, equation 5.1 was capable of predicting the trend of iodine desorption with good accuracy. In general, the desorption rate observed experimentally were much too slow to explain steady state situation. Hence, it can be deduced that, for most experiment, surface pseudo-saturation better explained the observed maximum loadings.
Similar behavior was observed for iodine deposition and desorption at high relative humidity. The rate of desorption was much lower than the value required for steady state to occur. For example, in an experiment with SS-316L at high iodine concentration (~10^-7 mol/L), high relative humidity, and a tube temperature of 23°C, the observed k_d was 0.29 cm/s. The calculated k based on the steady state assumption was 1.6x10^-3 s^-1 while the experimental value was 7.3x10^-4 s^-1 (Figure 5.13). As before, using a desorption rate constant based on the assumption of steady state over predicts the rate of desorption and surface pseudo-saturation is a more plausible interpretation.

![Graph](image)

Figure 5.13 Surface loading as a function of time at high humidity: experimental and equation 3.3 ([I2]_g = 10^-7 mol/L, T = 23°C, high relative humidity)

An example of desorption results that shows rapid iodine loss from the surface is shown in figure 5.6. This result suggests the possibility of iodine physical adsorption on the surface. The initial iodine loading was performed under high gas concentration (~10^-7 mol/L), low relative humidity and 23°C. Adsorption was found to be very rapid, quickly reaching a surface concentration higher than 10^-6 mol/cm^2. This value is approximately 1000 times the reported
value for monolayer coverage. Rapid desorption occurred when the relative humidity was
deliberately increased, even though the iodine concentration remained constant. An accurate
estimate of the desorption rate constant is difficult to obtain as there was a sudden jump in iodine
retention on tube surface. The rate of desorption, however, appeared to match that of adsorption.
A rough estimate of the iodine desorption rate from the surface gave a value on the order of $10^{-10}$
$\text{mol/cm}^2 \cdot \text{s}$. The associated rate of adsorption was approximately $10^{-10} \text{mol/cm}^2 \cdot \text{s}$ (at $k_d = 0.28$
$\text{cm/s}$).

It should be noted that the behavior observed in this experiment was quite unusual. The
adsorption rate was much higher than that observed in other experiments performed at high
iodine concentration with low relative humidity. In addition, desorption is usually more rapid
under dry conditions than humid conditions. This is the opposite of the trend seen in figure 5.6.
The experiments were repeated four times and the same behavior was always observed. It is
speculated that the iodine concentration used in this experiment may have been high enough to
produce multilayered physical adsorption. It should also be noted that these four experiments
were performed using steel provided by a different supplier than that used to obtain the tubing
used in all other tests.

5.4.1 Desorption Under Different Range of Humidity

Experiments were conducted to evaluate the effect of relative humidity on desorption
rate. Lower humidity was found to cause a higher rate of desorption. Figure 5.15 shows
desorption results for high relative humidity (>75%) and low relative humidity (<25%) at 40°C.
During the later stage of desorption, temperature was decreased to 23°C to see the effects of
lowering the temperature. Desorption occurred faster at low relative humidity. This was true for the two temperatures examined.

![Iodine Adsorption and Desorption](image)

Fig 5.15 Desorption under different relative humidities and tube temperatures (loading occurred for \([I_2]_g = 10^{-8}\) mol/L, \(T = 40^\circ\text{C}\), relative humidity as indicated in figure)

A similar trend was not observed at a tube temperature of 90°C, in that, the rate of desorption was unaffected by changes in relative humidity (figure 5.16). This further supports the previous assertions that at surface temperature of 90°C humidity played a less significant role in determining the interaction between iodine and the steel surface. An important observation is that the rate of desorption for this experiment was similar to that expected based on the steady state assumption. Given the observed deposition velocity of 0.1 cm/s and assuming a distribution coefficient of 1000 cm (figure 5.10) the desorption constant based on the steady state assumption would be \(10^{-5} \text{ s}^{-1}\). The observed value was approximately 3 times higher. This provides further support that at low concentration iodine retention occurred predominantly by physical adsorption.
Figure 5.16 Iodine desorption under different relative humidity at 90°C. Iodine loading involved $[I_2]_g = 3.5 \times 10^{-11}$ mol/L, low relative humidity and 90°C.

5.4.2 Desorption and Iodine Reloading

Most of the data for iodine deposition generated in this study only addresses short term adsorption. There is little data relevant to the long term impact of the interaction between the deposited iodine and the steel surface. However, a few experiments were carried out to investigate as to whether long term interactions would enhance further iodine deposition or inhibit the process.

Figure 5.17 Iodine Desorption and Reloading ($[I_2]_g > 10^{-7}$ mol/L, high relative humidity, 23°C).
An experiment was performed with a high iodine concentration (10^{-7} \text{ mol/L}) under high relative humidity with a tube temperature of 23^\circ\text{C}. Initial iodine deposition was rapid and a maximum loading approaching 1.2 \times 10^{-7} \text{ mol/cm}^2 was quickly achieved. Desorption, however, occurred at a much slower rate. Nearly three days were required for most of the iodine deposited to desorb from the surface. Following desorption, iodine reloading under similar gas phase conditions was attempted. Only negligible amounts of iodine were deposited during this reloading experiment. It appears that during desorption, some interactions between steel and iodine caused the steel surface to become much less susceptible to iodine deposition. Possibly, the change in the surface conditions of the steel was brought by some chemical interactions between iodine and the steel tube.

5.4.3 Volatilization of Iodine from FeI_2 Solution

Iodine may be physically adsorbed onto the steel or it may undergo chemical transformations through some chemical reactions with metal constituents of the steel. It is also possible that both phenomena occur on the surface, in other words, both physically and chemically adsorbed iodine may exist on the same steel surface. However, it is common sense that prior to any surface chemical transformation, the iodine must first be physically adsorbed by the surface.

If any chemical reactions occur on the surface, one likely product of the reactions would be I^- which is not volatile. Therefore, desorption of I^- directly from the surface is not possible. The desorption process may take place if the I^- is oxidized back into a volatile form i.e. I_2. To test whether such an oxidation process could take place additional experiments were performed.
Experiments were carried out by passing an air stream above 100 mL of a saturated $\text{FeI}_2$ solutions (figure 5.18). Any $\text{I}_2$ formed by the oxidation of $\text{I}^{-}$ in the first flask would be carried by the gas stream into the second flask. The second flask which contained 100 mL of 0.1 M NaI would trap the incoming $\text{I}_2$ by its reaction with $\text{I}^{-}$ to form $\text{I}_3^{-}$. Analysis was performed by spectrophotometric detection of $\text{I}_3^{-}$ which has strong absorptivity at 350 nm.

![Diagram](image)

Figure 5.18 Apparatus to study iodine volatilization from $\text{FeI}_2(aq)$.

The result which shows the amount of iodine detected in the second flask can be seen in the following figure.

![Graph](image)

Figure 5.19 Volatilization of iodine from $\text{FeI}_2$ solution.
Based on these results, iodine volatilization from FeI₂ solution is possible. The process involves the production of I₂ which is volatile and therefore can be released into the gas phase. The process that is responsible for the production of I₂, however, is not known. Initially it was thought that a reaction was occurring involving the conversion of Fe²⁺ to Fe³⁺ due to oxidation by O₂ with subsequent oxidation of I⁻ by Fe³⁺. However, when the air stream was replaced with N₂, a similar rate of I₂ production was observed which suggests that the availability of O₂ is not necessary for the process. The I₂ production was found to be reduced by lowering the concentration of FeI₂ in the original solution. In this experiment a saturated solution was diluted by a factor of four. The results however only showed a factor of two reduction in the production of I₂.

Based on the results on figure 5.18, it can be estimated that the rate of loss of I₂ from the 100 mL saturated FeI₂ solution was approximately 3x10⁻¹⁰ mol/s. This rate is actually faster than the desorption rate observed for any of the 26 cm² tube samples used in the study. However, it is not yet known if or how the I₂ loss depends on the solution volume. In addition, it is difficult to estimate the quantity of water on the tube samples. Hence direct comparison of the rate observed for these solutions and the desorption rate from the tube is not yet possible.

5.5 Iodine Retention on Compression Fittings

An additional experiment was carried out to examine the possible contribution of stainless steel fittings to the overall I₂ retention on stainless steel sampling lines. The experiment was performed by including a steel fitting at the middle of the steel tubing sample. The trend of
I$_2$ deposition with time as well as its distribution along the tubing are shown in figures 5.20 and 5.21.

Figure 5.20 Iodine deposition with time : SS-316L tube with stainless steel fitting at the middle ( [I$_2$]$_g$ = 3.5E-8 mol/L. T = 23 C. relative humidity = 85%).

The values of $k_d$ associated with the above duplicate experiments are 1.12x10$^{-1}$ cm/s for MC-1 and 4.9x10$^{-2}$ cm/s for MC-2. An interesting observation made is that in the above figure, a delay period which is usually absent at 23°C was observed. Furthermore based on the plot of I$_2$ distribution along tubing, most of the loading was due to I$_2$ accumulation on the middle part where the stainless steel fitting was attached (figure 5.21). The body of the fitting itself only retained small a amount of I$_2$. The highest retention appeared to be on the part of the tubing that was attached to the steel fitting. Possibly the high retention of iodine on this part was due to the damage to the steel surface caused by cutting and smoothing. Additionally, the increased turbulence in the region may have further increased the retention. Another observation based on the data is that the extent of the damage on the tubing may be different given that the amount of retention at all the tube ends are different. For example, the part attached to the teflon fitting (2.5
cm and 24.5 cm) seemed to retain substantially less I$_2$ compared to the part attached to the steel tubing.

![Distribution of Iodine Activity Along Tubing](image)

**Figure 5.21** Distribution of iodine activity along the tubing

Based on this result, care should be taken in relation to the sections of sample lines where damage to the surface may exist, such as the damage made by cutting. One possible solution is to chemically treat the surface by immersing the steel in HNO$_3$ solution to recover the damage oxide film and repassivate the steel surface. The high retention at tube ends also supports the theory of increasing iodine retention due to chemical interaction at locations where surface defects exist.

Throughout the experiments, higher I$_2$ retention at the inlet and outlet were observed. In all of these experiments, teflon fittings were used to connect the steel sample to the teflon tubing that carried the gas stream. Other than the inlet and the outlet parts, the rest of the tubing showed reasonably even I$_2$ distribution along the length. The plots of iodine distribution along the tubing are included in appendix A.
5.6 Possible Mechanisms

Upon reviewing the observed trends of deposition under various operating conditions, it is now possible to speculate in regards to the possible mechanisms behind the retention of iodine on stainless steel. The mechanisms for iodine deposition can be divided into three different categories. The first one involves physical adsorption of I\(_2\) which in general predominates at low iodine concentrations. The second is a slow chemisorption process that occurs under dry conditions with higher iodine concentration. The third is a rapid corrosion based chemisorption of I\(_2\). As this process requires the presence of water to occur, it only occurs under medium to high relative humidity conditions, with higher iodine concentrations.

5.6.1 Physical Adsorption

Some theoretical consideration of physical adsorption is discussed on section 2.4.1.

\[ I_{2(g)} \leftrightarrow I_{2(s)} \]  
(R 5.1)

Physical adsorption involves weak or indirect bonding between the iodine molecules and the steel surface. This attractive force is opposed by the concentration gradient generated by the accumulation of iodine on the surface. Hence, after a certain period of loading, the surface may achieve a steady state. Therefore, it should be expected that the observed deposition rate would be initially high. The rate will decrease as steady state is approached. To predict the variation of iodine surface concentration as a function of time, equation 2.3 is appropriate. Another characteristic of physical adsorption is the relatively high desorption rate compared to chemical adsorption. Finally, multilayered physical adsorption is only expected for partial pressures of the same order of magnitude as the vapor pressure of the compound.
Based on the data obtained, physical adsorption predominated for iodine concentrations below approximately $10^{-9}$ mol/L. This upper limit corresponds to a surface loading of $10^{-9}$ mol/cm$^2$, given the observed distribution coefficient of 1000 cm (figure 5.10). Hence, it appears that physical adsorption alone occurred for loadings below that expected for monolayer coverage.

### 5.6.3 Slow Chemisorption

A different behavior of iodine deposition was observed at gas concentration higher than $10^{-9}$ mol/L and low relative humidity. The same anomaly was also observed for high relative humidity and a tube surface temperature of 90°C. The deposition was characterized by a slower $k_d$ compared to other experimental conditions (figure 5.1). In fact if deposition rate is plotted as oppose to $k_d$, it can be seen that the rate of iodine deposition appeared to be relatively constant regardless of the gas phase concentration or temperature (figure 5.22). This trend could only be seen for SS-316L. For SS-304L, no clear trend was evident (figure 5.23).

![Iodine Deposition Rate Vs $[I_2]_g$](image)

**Figure 5.22** Iodine deposition rate ($N_d$) as a function of gas concentration (SS-316L)
Figure 5.23 Iodine deposition rate ($N_d$) as a function of gas concentration (SS-304L)

Further analysis of the data suggests that physical adsorption is not the phenomena behind the deposition. Unlike physical adsorption which predominantly occurs at gas concentration below $10^{-4}$ mol/L, the value of $K_D$ was found to be between 10 cm and 100 cm (figure 5.10). Below $10^{-4}$ mol/L, for physical adsorption, $K_D$ was found to be approximately 1000 cm. This suggests that the maximum loading is not determined by the balance between $I_2$ on the surface and $I_2$ in the gas phase. Furthermore, desorption data shows that the desorption rate was much slower than the rate of adsorption (e.g. figure 4.12). This indicates that the $I_2$ may have been chemically adsorbed on to the steel. It should be noted, however, that desorption data was very limited. Further investigation is required.

Another observation made was that, for the case of slow chemisorption, $k_d$ may not be appropriate. In the use of $k_d$, it is implicitly assumed deposition rate is a first order function of gas phase concentration. As can be seen in figure 5.22, iodine deposition rate appeared to be constant despite the change in gas concentration. Possibly the rate of reactions on the surface was governed by the amount of physically adsorbed iodine which was limited to one monolayer.
(10^{-6} \text{ mol/cm}^2). Hence, within the region where slow chemisorption predominates, deposition rate \( (N_d) \) is suggested to be used to replace \( k_d \). As to the nature of the reactions that occur on the surface, the information obtained is not adequate to allow any speculation. Further study in this matter is needed.

5.6.3 Iodine Chemisorption with Corrosion

The third process is iodine chemisorption with corrosion of the steel surface. Throughout the presentation of results, it has been observed that humidity plays a significant role in affecting the rate and extent of iodine deposition on stainless steel. This suggests that chemical reactions on the surface are greatly accelerated by the presence of water. Several authors such as Deir and Tsukaue et.al \([7, 8, 9]\) have proposed interactions which involve pitting corrosion attack of steel by iodine. For such corrosion reaction, the presence of water on the surface is necessary to facilitate the electrochemical reaction.

The process of chemisorption is usually preceded by physical adsorption. Initially, \( I_2 \) may be physically adsorbed onto the metal surface or it may also be adsorbed into water micro-droplets that may exist on the surface. The adsorption of \( I_2 \) into water droplets on stainless steel has been observed by Tsukaue et.al. \([8]\). In this investigation, similar condensation of water which adsorbed \( I_2 \) was also observed. Any \( I_2 \) deposited near surface defects will react with the steel to form \( I^- \). Most probably, \( I_2 \) will first react with the most reactive component of the steel i.e. Fe. Comparison of reactivity with iodine among the three major metal constituents of stainless steel namely Fe, Ni and Cr shows that Fe is the most prone to the chemical attack, followed by Ni and then Cr \( \text{table 3.5} \). The same data shows that Cr is largely unreactive with \( I_2 \).
This coincides with the fact that the oxide film of Cr is mainly responsible for the stainless quality of the steel. For stainless steel to remain passive, the level of Cr as defined by the bulk concentration must be maintained throughout the entire metal matrix. If local regions exist where the chromium concentration is depleted, these regions will become susceptible to localized corrosion [37]. The surface, however, may become repassivated through the dissolution of the most reactive component, i.e. Fe, with the consequence of Cr enrichment of the steel surface which may lead to a renewed stainless quality [4].

The following reactions have been suggested as the possible mechanisms of interactions between Fe and I₂ [1]. As the reactions require the presence of water, it is implicitly assumed that some water already exists within the surface defects thus making it possible for the reaction to be initiated.

1) Adsorption of I₂(g) on to the surface or water droplets:

\[ \text{I}_2(g) \leftrightarrow \text{I}_2(s) \quad (R \ 5.1) \]

\[ \text{I}_2(g) \leftrightarrow \text{I}_2(aq) \quad (R \ 5.2) \]

2) Electrochemical reactions between I₂ and Fe:

\[ \text{Fe}^{2+}_{(aq)} + 2e^- \leftrightarrow \text{Fe}_{(s)} \quad (-0.44 \text{ V}) \quad (R \ 2.1) \]

\[ \text{I}_2(g) + 2e^- \leftrightarrow 2I^- \quad (-0.535 \text{ V}) \quad (R \ 2.2) \]

Combining the two reactions will give:

\[ \text{Fe}_{(s)} - \text{I}_2(g) \leftrightarrow \text{Fe}^{2+}_{(aq)} + 2I^-_{(aq)} \quad (-0.975 \text{ V}) \quad (R \ 2.3) \]

3) The resulting Fe²⁺ ions may react with O₂ diffusing from the gas phase giving the final corrosion products Fe₂O₃:

\[ 4\text{Fe}^{2+}_{(aq)} + \text{O}_2 + (4+2x)\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}_{(s)} + 8\text{H}^- \quad (R \ 2.4) \]
Another observation made during the investigation is that no Fe$^{3+}$ was found in the wash solution from the inside surface of the tubing. This is possible as the formation of Fe$^{3+}$ may be prevented by I$^-$ through the following reaction:

$$\text{Fe}^{2+}_{\text{aq}} + \text{I}^-_{\text{aq}} \leftrightarrow \text{Fe}^{3+}_{\text{aq}} + \text{I}_2(\text{aq}) \quad (R \ 5.3)$$

Reaction 5.3, however, may occur during desorption in that Fe$^{2+}$ may be oxidized to Fe$^{3+}$ which subsequently reacts with I$^-$ to produce I$_2$ which desorbed from the surface. Once the majority of I$^-$ has been removed from the surface, Fe$^{3+}$ may exist and form a protective oxide layer.

The above reactions suggest a deposition mechanism involving the oxidation of Fe to Fe$^{2+}$ by I$_2$. Based on this hypothesis, it can be deduced that the amount of iodine adsorbed by the steel surface, which is reflected by the magnitude of $k_d$ and $C_i^o$, may depend on several factors such as the number of available sites to initiate the reactions and how well these sites will propagate under the relevant experimental conditions. Additionally, the rate may also be affected by the properties of the corrosion products formed on the surface of the steel.

As indicated above, the number of initiation sites may affect iodine retention on the steel surface. These sites are locations where defects exist in the protective oxide layer. The number of sites available may be a property specific to any tubing particularly with respect to its manufacturing history. For example, Lee et.al [26] observed differences in iodine deposition behavior in stainless steels originated from two different manufacturers. Corrosion reactions in these initiation sites may lead to localized reactions which, in the end, leads to pitting corrosion. These sites, however, may not all propagate. Some would cease to grow if the necessary conditions for growth are not satisfied. Tsukaue et.al. [9] have observed a period of delay before pitting corrosion occurs. Moreover, based on their observation, not every initiation site can
propagate. According to their observation, only pits with depth > 0.1 mm would grow stably under environment containing I₂. Among the factors that can affect the probabilities of pit propagation are gas relative humidity, tube surface temperature and, possibly, iodine concentration.

Gas phase humidity will affect the corrosion reactions by supplying the surface with the required water. It can therefore be expected that, at high humidity, iodine retention would be high. This phenomenon has been confirmed by the experimental results. Furthermore, the FeI₂ salt produced is hygroscopic in nature. Hence, it will cause further condensation on the steel surface. Due to its hygroscopic nature the salt will also improve the stability of the water already existing on the surface. The enhanced presence of water on the surface will further increase the corrosion attack by iodine on the steel surface.

Tube surface temperature will affect the reactions in several ways. By increasing the temperature, the rate of any chemical reactions may be increased. Furthermore, pitting probability will also increase at higher temperature. If the temperature is increased sufficiently, however, the amount of surface water will be reduced as more water will be driven off the surface due to evaporation. Moreover, increased temperature will decrease I₂ physical adsorption. Thus, it should be expected that increasing temperature may initially increase I₂ retention (<60°C as found in the current study). When the temperature is sufficiently high as to substantially reduce the amount of surface water, the iodine retention should also be reduced.

The effect of both temperature and relative humidity were relatively weak at low iodine concentration. This can be explained in terms of the small loading of I₂ on the surface. It is speculated that at low iodine loadings, the amount of iodine present on the surface was
inadequate to allow the rapid propagation of the corrosion reaction. As a result, the amount of FeI₂ formed was low and insufficient to substantially increase the presence of water on the surface.

The situation is different under higher gas concentration. Higher amounts of iodine are deposited with the consequence of higher amounts of hygroscopic FeI₂ on the surface. The amount of condensing water will also be greater as to commence the corrosion cycle: producing more FeI₂ and condensing more water from the gas phase. This interpretations implies the existence of a critical relative humidity (RHₜₕᵣₖ) which is likely quite low given the hygroscopic nature of FeI₂. If the gas phase relative humidity is reduced to a value below the critical value, the amount of water condensing would be suppressed such that further production of FeI₂ salt would also be inhibited. In this investigation, the specific value of RHₜₕᵣₖ was not identified. The value may, in fact, depend on several factors such as tube surface temperature. Results obtained point out that RHₜₕᵣₖ may be higher than 25%. Deir [7] also found that iodine deposition behavior at medium relative humidity (~50%) is similar to the behavior at high relative humidity (>75%). Hence, it is possible that RHₜₕᵣₖ may lie between 25% to 50%.

The parameter used to describe the extent of iodine deposition is the pseudo-saturation surface concentration (Cₛ⁰). The magnitude of Cₛ⁰ appears to be determined by the capability of the corrosion sites to propagate. As in the above discussion, the extent of propagation will be dictated by the provision of the conditions that would support corrosion reactions. It is for these reasons that the value of maximum loading differs depending on the relevant operating conditions. It is therefore likely that Cₛ⁰ is not surface saturation but rather the point where the surface reactions cease to propagate. This is consistent with the observation of declining
deposition rate as $C_s^\infty$ is approached. Conditions such as warm temperature (40°C to 60°C), high relative humidity and high iodine gas phase concentration would cause high iodine deposition on the steel surface. While low relative humidity, low iodine gas phase concentration and high tube surface temperature will yield a lower value of $C_s^\infty$.

The corrosion reactions that occur on the surface will eventually produce some form of metal oxides such as iron oxides. The properties of the surface will to some extent be determined by the physical properties of this film of corrosion products. Metal oxides are generally not soluble in water. Therefore unlike FeI₂, it will not cause further condensation of water. If the film is porous in nature, despite the formation of this film, I₂ from the gas phase may still diffuse through the matrix of corrosion products at a reasonable rate and finally react with Fe atoms. On the other hand, the film may have low porosity, increasing the resistance for diffusion of I₂ on the surface. This may eventually lead to a decrease in the number of sites available for chemisorption on the surface limiting the propagation of the corrosion.

This interpretation is consistent with the observed trends. The highest iodine deposition was observed at high humidity and tube surface temperature between 40°C and 60°C. Presumably at this temperature the presence of water on the surface was still adequate while the warm temperature served to increase I₂ corrosion of the surface as well as increasing the vulnerability of the steel to pitting corrosion attack. When the temperature was increased to 90°C, the rate as well as the extent of iodine deposition were reduced. In fact, at this temperature, humidity seems to have no impact on iodine deposition. Water condensation was suppressed and the chemical reactions on the steel surface were also inhibited.
C₅° was not observed when the experiment was conducted at high gas concentration (>5x10⁻⁸ mol/L), high relative humidity and tube temperatures of 40°C or 60°C. Iodine accumulation continued to climb at a high rate even though the surface concentration was already higher than 10⁻⁷ mol/L. Hence, it appears that under these conditions, the process of pitting corrosion was able to propagate stably. The conditions seemed to be sufficient to commence the cycle between the production of hygroscopic FeI₂ and the condensation of water. The warm temperature likely increased the rate of reactions as well as increasing the steel susceptibility to pitting corrosion attack by iodine. Additionally, Cr dissolution from steel surfaces in saturated solutions of I₂ at temperatures between 30°C and 60°C has also been observed [8]. The oxide film of Cr is mainly responsible for the passivity of stainless steel surface. It may be that at 40°C or 60°C, this protective layer was broken down by a solution containing I₂ then the steel would have lost its inert property.

From the experiment with iodine reloading which was carried out after a substantial amount of iodine desorbed from the surface, the failure of reloading may have been caused by a protective layer of oxide scale forming on the surface. The scale may have created higher resistance to iodine diffusion to reach any reactive sites underneath. Even if the scale was initially porous in nature, it is possible that during the desorption process the surface was given a period of time to precipitate more iron oxides which eventually sealed the pores. Furthermore, any exposed reactive sites on the surface would have been consumed and subsequently covered by either the inert layer of corrosion products or passivated through Cr enrichment of the surface. In other words, the desorption process provided the steel surface with the needed time to develop
its protective oxide film. Similar sealing of the pores may also occur during the period of deposition hence lowering the value of $k_d$.

It should be noted, however, the current investigation did not include any visual examination of the steel surface. This hypothesis was simply developed based on the observation of $k_d$ and $C_v$ as well as the information available in the literature. It is recommended that the steel surface be studied visually under magnification to observed the changes in the properties of the steel due to iodine deposition.

Therefore, in summary, the rate and extent of the reactions between $I_2$ and Fe will be determined by several factors which include:

1. The number of reactive sites originally present on the steel surface: This number will be dictated by the manufacturing history of the steel sample.

2. The combined effects of tube surface temperature and relative humidity: these two factors will determine whether the corrosion sites will grow in a stable manner thus causing more iodine to deposit and react on the surface.

3. The iodine gas phase concentration: Gas concentration will affect the retention through the deposition of iodine and the subsequent formation of hygroscopic $FeI_2$. This hygroscopic property reduces the necessary relative humidity to cause water condensation which in effect will assist the formation of more $FeI_2$. The hygroscopic effect, however, may only be effective if the surface concentration surpasses a certain critical value

4. The cycle of reactions may be stopped if the necessary conditions required for them to propagate are not satisfied. Furthermore, the formation of corrosion product scale on the surface may increase the resistance for iodine diffusion to reactive sites beneath the scale.
5.7 Applications to Gas Sampling Lines

The following table summarizes the values the deposition parameters observed under various operating conditions. These values give a general indication of the behavior under the specified condition. However, as can be seen from figures 5.1, 5.3, 5.9 and 5.10, some exceptions did occur.

Table 5.6 Expected iodine deposition parameter values for stainless steel lines

<table>
<thead>
<tr>
<th>[I$_2$]$_e$ mol/L</th>
<th>Relative Humidity</th>
<th>Tube Temp. (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>$C_s^o$ (mol/cm$^2$)</th>
<th>$K_D$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 10$^{-9}$</td>
<td>Low/High</td>
<td>23 - 90</td>
<td>10$^{-2}$ - 10$^{-1}$</td>
<td>10$^{-10}$ - 10$^{-9}$</td>
<td>~1000</td>
</tr>
<tr>
<td>10$^{-9}$ - 10$^{-7}$</td>
<td>Low</td>
<td>23 - 90</td>
<td>10$^{-14}$ - 10$^{-12}$ mol/cm$^2$.s (a)</td>
<td>10$^{-9}$ - 10$^{-8}$</td>
<td>-</td>
</tr>
<tr>
<td>&gt; 10$^{-7}$</td>
<td>High</td>
<td>23</td>
<td>&gt; 10$^{-1}$</td>
<td>~10$^{-7}$</td>
<td>-</td>
</tr>
<tr>
<td>&gt; 10$^{-7}$</td>
<td>High</td>
<td>40 - 60</td>
<td>&gt; 10$^{-1}$</td>
<td>~10$^{-8}$</td>
<td>-</td>
</tr>
<tr>
<td>&gt; 10$^{-9}$ (316 L)</td>
<td>High</td>
<td>90</td>
<td>&lt; 10$^{-2}$</td>
<td>~10$^{-8}$</td>
<td>-</td>
</tr>
<tr>
<td>&gt; 10$^{-9}$ (304 L)</td>
<td>High</td>
<td>90</td>
<td>~10$^{-1}$</td>
<td>~10$^{-8}$</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) $k_d$ under these condition was not appropriate (see section 5.2). Therefore, deposition rate (mol·cm$^{-2}$.s) is used instead.

The following assessment is carried out using the case of flow rates of 1.5 L/min, 4.5 L/min and 12 L/min with a line length of 10 m. If the atmospheric conditions during the use of the sample line is humid and warm (40°C - 60°C), the highest losses of iodine should be expected. If iodine retention associated with pitting corrosion continues to propagate, with the relevant values of $k_d$ on the order of 10$^{-1}$ cm/s, practically no iodine will make it through the sampling lines. A more credible accident situation would yield iodine concentration of 10$^{-9}$ mol L or lower. Values in table 5.6 above are used to generate figure 5.24. Gas concentration is
assumed to be $10^{-9}$ mol/L while $k_d$ is assumed to be $5 \times 10^{-2}$ cm/s. From $K_D$ equals to 1000 cm, a value of $C_s^o$ near $10^{-9}$ mol/cm$^3$ can be assumed. Furthermore, the assumption of steady state (equation 2.3) gives a value of $k$ of $5 \times 10^{-5}$ s$^{-1}$.

![Iodine Transmission Fraction Vs Time](image)

**Figure 5.24** Variation of iodine transmission fraction with time

As can be seen above, transmission fraction is initially low but increases as the surface is gradually loaded. Eventually, the transmission fraction will asymptotically approach 100%. It can also be seen that increasing the flow rate can substantially increase the transmission fraction. For comparison, table 5.8 summarizes the values of transmission fraction as calculated by equation 2.16. Equation 2.16 will only predict a single value of iodine transmission fraction. Similarly, equation 2.16 also predicts higher iodine transmission fraction at higher flow rate.

**Table 5.7** Estimated iodine transmission fraction based on equation 2.16

<table>
<thead>
<tr>
<th>$k_d$ (cm/s)</th>
<th>Volumetric Flow rate</th>
<th>Transmission Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>1.5 L/min</td>
<td>5%</td>
</tr>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>4.5 L/min</td>
<td>37%</td>
</tr>
<tr>
<td>$5 \times 10^{-2}$</td>
<td>12 L/min</td>
<td>69%</td>
</tr>
</tbody>
</table>
A similar behavior of increasing iodine transmission fraction with time has been observed by Edson et al. [6]. Their report is summarized in Table 3.4. The effect of increasing flow rate has to some extent been confirmed by a test performed by Ontario Hydro. The test was performed on November 30, 1992 (Table 3.11). By increasing the flow rate, the transmission fraction was also increased. Based on the same set of test results, the trend of iodine loss with time, however, seemed to contradict the results shown on Figure 5.24. Iodine loss within subsequent tests was increasing. The trend of increasing iodine loss over time may have been a result of the conditions used. The gas concentration was on the order of $10^{-8}$ mol/L while the humidity was likely ambient (>50%). Under these conditions $k_d$ for SS-304L may have been initially low (Figure 5.9). However, the iodine deposited during the first few tests may have been adequate to form FeI$_2$, thereby initiating the corrosion cycle, and increasing $k_d$. 
6. Conclusions and Recommendations

6.1 Conclusions

1. It is believed that I₂ is deposited through both physical and chemical adsorption. Physical adsorption predominated at gas concentrations below 10⁻⁹ mol/L. Under this condition kₐ was found to be between 10⁻² to 10⁻¹ cm/s. A distribution coefficient (Kᵣ) of approximately 1000 cm was observed. The highest maximum loading observed in this condition was on the order of 10⁻⁹ mol/cm².

2. At gas concentration higher than 10⁻⁹ mol/L at low relative humidity, slow chemisorption appeared to be responsible for iodine deposition. The trend was characterized by a slow but relatively constant iodine deposition rate (10⁻¹³-10⁻¹⁴ mol/cm².s). Deposition velocity (kₐ) is not appropriate to be used under this condition as it appears to vary with gas concentration. The maximum loading was between 10⁻⁹ to 10⁻⁸ mol/cm².

3. At gas concentration higher than 10⁻⁹ mol/L and high humidity, a pitting corrosion type chemisorption mechanism may have enhanced deposition. The deposition velocity was on the order of 10⁻¹ cm/s. Possibly the rate close to being limited by gas side mass transfer. I₂ is believed to have reacted with the steel at defect sites to form hygroscopic FeI₂. FeI₂ attracted more water facilitating the propagation of the corrosion reaction. Under some conditions, the propagation was inhibited resulting in an apparent maximum surface loading (Cₐ°). However, at temperature of 40°C or 60°C, no such inhibition occurred resulting in very rapid iodine adsorption. A slow initial deposition rate that might be associated with pitting incubation period was observed.
4. Despite the expectation that SS-316L should perform better, particularly under medium and high gas concentration, there appeared to be no difference between the two types of steel. In fact, some results suggest that SS-304 performed better than SS-316L. Under low gas phase concentration, however, most of the results for SS-316L were below detection limit, suggesting that SS-316L would perform better under low iodine concentration. The most likely concentration in an accident condition would be within the low range (<10⁻⁶ mol L⁻¹). Therefore the use of SS-316L may be justified. This trend, however, should still be confirmed. A different method of gaseous iodine generation may be required as to enable the use of higher iodine specific activity.

5. Attention should be given to minimizing any damage to the steel surface prior to its installation in radioiodine sampling lines. Iodine retention may be accelerated in regions where damage to the protective oxide layer exists. This is especially true for regions such as the inlet and outlet where damage may occur during the cutting of the steel tubing. Additionally, the initial steel surface conditions may also affect iodine retention. This may depend on the manufacturing history of the steel tubing.

6.2 Recommendations

1. To obtain more evidence on the occurrence of corrosion of the steel by I₂, visual magnification of the conditions of the surface after its exposure to iodine should be performed. This will provide more evidence on the occurrence of corrosion reactions due to attack by iodine. Specifically, attention should be placed on whether pitting actually occurs on the surface. The physical appearance as well as chemical composition of the corrosion
products, if any, should also be examined. An oxide layer that is porous in nature would provide pathways for the iodine to diffuse and reach an exposed Fe atom. Identification of the reaction products accumulated on the surface should also be performed. The recognition of the chemical compound formed would further corroborate mechanisms that are proposed for the corrosion enhanced deposition. Furthermore, such study would also provide some insight into the possible mechanisms responsible for the slow chemisorption phenomenon.

2. It is speculated that one of the factors that causes the pitting corrosion to cease to propagate is the enrichment of the steel surface with Cr after the dissolution of the more reactive component of the metal matrix such as Fe. Confirmation of this hypothesis can be obtained by studying the metal composition of the surface after the corrosion product is removed.

3. This research effort placed more emphasis on studying the phenomena of iodine deposition. Very limited data was obtained on the desorption process. More data is required to confirm the different mechanisms proposed in this report. For physical adsorption, for example, desorption rate would be sufficiently fast to match the deposition rate observed in the beginning of the loading. For chemisorption, desorption rate would be much slower compared to the rate of adsorption.
7. References:


24. Funke, F. and Hellmann, S. “Reaction of Iodine with Steel Surfaces, Part 2: Assessment of Iodine Steel Interactions and Experimental Study.” EUR 15668. 2 EN.


8. Nomenclature

\(C_g\) = iodine gas phase concentration (mol/cm\(^3\)).
\(C_{g1}\) = iodine gas phase concentration at outlet (mol/cm\(^3\)).
\(C_{g0}\) = iodine gas phase concentration at inlet (mol/cm\(^3\)).
\(C_s\) = iodine surface concentration (mol/cm\(^3\)).
\(D\) = tube inside diameter (cm).
\(D_{AB}\) = binary diffusion coefficient (cm\(^2\)/s).
\(F\) = volumetric flow rate (cm\(^3\)/s).
\(f\) = iodine transmission fraction.
\(k\) = desorption rate constant (s\(^{-1}\)).
\(k_d\) = deposition velocity (cm/s).
\(K_d\) = distribution coefficient (cm).
\(k_z\) = gas phase mass transfer coefficient (cm/s).
\(k_s\) = surface adsorption rate coefficient (cm/s).
\(L\) = tube length (cm).
\(N_g\) = iodine deposition rate (mol/cm\(^2\).s).
\(N_s\) = iodine desorption rate (mol/cm\(^2\).s).
\(Re_D\) = Reynolds number for flow through the tube.
\(RH\) = relative humidity (%).
\(RH_{crit}\) = critical relative humidity (%).
\(Sc\) = Schmidt number.
\(Sh_D\) = Sherwood number.
\(T\) = temperature (°C or Kelvin).
\(V\) = gas linear velocity (cm/s).
\(\rho\) = density (g/cm\(^3\)).
\(\nu\) = kinematics viscosity (cm\(^2\)/s).
\(\mu\) = viscosity of the gas (kg/m.s).
\(\mu_s\) = viscosity of the gas near the wall (kg/m.s).
APPENDIX A - DATA PLOTS

Stainless Steel 316L  page 106-144
Stainless Steel 304L  page 145-172
23 C - HIGH [I\(_2\)]g - HIGH RH

MAY 4, 95 - 1

SS-316 / 23 C
HIGH RH / HIGH [I\(_2\)]

DESORPTION

iodine (mol/cm\(^2\))

[I\(_2\)] gas phase Conc.

mol/L

RELOADING

[I\(_2\)] mol/cm\(^2\)


mol/L

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

cm FROM INLET

800

600

400

200

0

5

10

15

20

25

0

5

10

15

20

25

IODINE DISTRIBUTION ALONG TUBING
(JULY 21-1 and JULY 21-2; SEE PAGE A4 FOR IODINE DISTRIBUTION ALONG THE TUBING)
**40°C - HIGH %RH - LOW [I\(_2\)]g**

**SS-316L / 40°C**

- RH: LOW-MED-HIGH / LOW [I\(_2\)]g

<table>
<thead>
<tr>
<th>TIME (min)</th>
<th>IODINE (mol/cm(^2))</th>
<th>[I(_2)]g mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0E-11</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>2.0E-12</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>3.0E-12</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>4.0E-12</td>
<td></td>
</tr>
</tbody>
</table>

**IODINE DISTRIBUTION ALONG TUBING**

- IODINE (dpm)

<table>
<thead>
<tr>
<th>cm FROM INLET</th>
<th>IODINE (dpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>
40 C - LOW %RH - MED [I2]g

IODINE DISTRIBUTION ALONG TUBING

IODINE (mol/cm²) vs TIME (min)

IODINE (dpm) vs cm FROM INLET
40 C - LOW %RH - LOW [I2]g

SS-316L / 40 C
LOW %RH / LOW [I2]g

Iodine (mol/cm²)^2

-[I2]g mol/L

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

cm FROM INLET
60 C - HIGH %RH - HIGH \([\text{I}_2]\)g

MAY 8, 96 - 1
SS-316L / 60 C
HIGH %RH / HIGH \([\text{I}_2]\)g

IODINE (mol/cm\(^2\))

Iodine (mol/cm\(^2\))

\([\text{I}_2]\)g mol/L

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

0 5 10 15 20 25
cm FROM INLET

1.0E+00
1.0E+02
1.0E+04
1.0E+06

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

0 5 10 15 20 25
cm FROM INLET

1.0E+00
1.0E+02
1.0E+04
1.0E+06
60 C - HIGH %RH - MED $[\text{l}_2]$g

July 22, 96 - 1

SS-316L / 60 C
HIGH %RH / MED $[\text{l}_2]$g

Iodine (mol/cm$^2$)

- 1.2E-08
- 1.0E-08
- 8.0E-09
- 6.0E-09
- 4.0E-09
- 2.0E-09
- 0.0E+00
- 2.0E-09

IODINE (mol/cm$^2$)

- 2.0E-08
- 1.8E-08
- 1.6E-08
- 1.4E-08
- 1.2E-08
- 1.0E-08
- 8.0E-09
- 6.0E-09
- 4.0E-09
- 2.0E-09
- 0.0E+00

TIME (min)

0 50 100 150 200 250

60 C - HIGH %RH - MED $[\text{l}_2]$g

July 22, 96 - 2

SS-316L / 60 C
HIGH %RH / MED $[\text{l}_2]$g

Iodine (mol/L)

- 1.6E-08
- 1.4E-08
- 1.2E-08
- 1.0E-08
- 8.0E-09
- 6.0E-09
- 4.0E-09
- 2.0E-09
- 0.0E+00

IODINE (mol/L)

- 1.2E-09
- 1.0E-09
- 8.0E-10
- 6.0E-10
- 4.0E-10
- 2.0E-10
- 0.0E+00
- 2.0E-10

TIME (min)

0 50 100 150 200 250

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

- 40,000
- 20,000
- 0

IODINE (dpm)

- 4000
- 2000
- 0

cm FROM INLET

0 5 10 15 20 25
60 C - HIGH %RH - LOW [I2]g

JULY 2, 96 - 1
SS-316L / 60 C
HIGH %RH / LOW [I2]g

IODINE (mol/cm²)

[12]g mol/L

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

cm FROM INLET
90°C - HIGH %RH - MED [I₂]ₘₚₙ

MAY 23, 96 - 2
S.S. 316L / 90C
HIGH RH / MED [I₂]ₘₚₙ

IODINE (mol/cm²)

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

cm FROM INLET
90°C - HIGH %RH - LOW [I₂]g

MAR 21, 96 - 1
SS-316L / 90 C
RH: LOW-MED-HIGH / LOW [I₂]g

IODINE (mol/cm²)

4.0E-11 Iodine (mol/cm²)
3.0E-11
2.0E-11
1.0E-11
0.0E+00
-1.0E-11
-2.0E-11
-3.0E-11
-4.0E-11

MARCH 21, 96 - 2
SS-316L / 90 C
RH: LOW-MED-HIGH / LOW [I₂]g

IODINE (mol/cm²)

6.0E-11 Iodine (mol/cm²)
5.0E-11
4.0E-11
3.0E-11
2.0E-11
1.0E-11
0.0E+00

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

3000
2000
1000
0

cm FROM INLET

0 5 10 15 20 25
90°C - HIGH %RH - LOW [I₂]₀
JULY 2, 98 - 2
SS-315L / 90C
HIGH RH / LOW [I₂]₀

IODINE [mol/cm²]
0.0E+00
-5.0E-11
-1.0E-10
-1.5E-11
0
180
200
300
400
TIME (min)

I₂ gas conc. (mol/L)
1.0E-10
1.5E-10
2.0E-10
2.5E-10
3.0E-10
5.0E-11
10E-11

IODINE DISTRIBUTION ALONG TUBING
dpm
0
20
40
5
10
15
20
25
cm FROM INLET
23°C - LOW %RH - MED [I₂]g

JULY 1, 96 - MC 1

SS-304L / 23 C
LOW RH / MED [I₂]g

[IODINE] mol/cm²

RUN STARTED

Iodine (mol/cm²)
- [I₂] gas phase Conc. mol/L

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

IODINE ACTIVITY (dpm)

cm FROM INLET
23°C - LOW %RH - MED [I$_2$]$_g$

JULY 1, 96 - MC2

SS-304L / 23 C
LOW RH

IZ gas conc. mol/L

[I$_2$]$_g$ gas phase Conc. mol/L

RUN STARTED

IODINE DISTRIBUTION ALONG TUBING

IODINE ACTIVITY (dpm)

cm FROM INLET
40°C - HIGH %RH - HIGH [I₂]g
MAY 3, 96 - 1
SS-304L / 40°C
HIGH RH

40°C - HIGH %RH - HIGH [I₂]g
MAY 3, 96 - 2
SS-304L / 23°C
HIGH RH

IODINE DISTRIBUTION ALONG TUBING
IODINE (dpm)
0 5 10 15 20 25
cm FROM INLET

IODINE (mol/cm²)
0.0E+00 1.0E-07 2.0E-07 3.0E-07 4.0E-07 5.0E-07 6.0E-07 7.0E-07 8.0E-07
TIME (min)

IODINE (mol/L)
0.0E+00 1.0E-07 2.0E-07 3.0E-07 4.0E-07 5.0E-07 6.0E-07 7.0E-07
TIME (min)
40°C - HIGH %RH - LOW [I₂]g
JUNE 26, 96 - 2
SS-304L / 40C
HIGH %RH / LOW [I₂]g

IODINE (mol/cm²)

[0.0E+00, 4.5E-10, 4.0E-10, 3.5E-10, 3.0E-10, 2.5E-10, 2.0E-10, 1.5E-10, 1.0E-10, 5.0E-11, 0.0E+00 -5.0E-11]

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

[0, 3000, 1500, 0]

cm FROM INLET

[0, 5, 10, 15, 20, 25]
40°C - LOW %RH - HIGH [I\(_2\)]g

Aug 27, 1996 - 1

SS-304L / 40 C
LOW RH / HIGH [I\(_2\)]g

[IODINE] mol/cm\(^2\)

-5.0E-10
0.0E+00
5.0E-10
1.0E-09
1.5E-09
2.0E-09
2.5E-09
3.0E-09

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

0 5 10 15 20 25 cm FROM INLET

IODINE (mol/cm\(^2\))

IODINE (mol/L)

MAY 7, 96 - 1

SS-304L / 40 C
LOW RH / MED [I\(_2\)]g

40°C - LOW %RH - MED [I\(_2\)]g

[IODINE] mol/cm\(^2\)

-5.0E-10
0.0E+00
5.0E-10
1.0E-09
1.5E-09
2.0E-09
2.5E-09
3.0E-09
4.0E-09
5.0E-09
6.0E-09
7.0E-09
8.0E-09

TIME (min)

IODINE DISTRIBUTION ALONG TUBING

0 5 10 15 20 25 cm FROM INLET

IODINE (mol/cm\(^2\))

IODINE (mol/L)
60°C - HIGH %RH - MED [I₂]g

FEB 28 1996 - 1
SS-304L / 60°C to 40°C
HIGH %RH / MED [I₂]g

IODINE (mol/cm²) vs TIME (min)

IODINE DISTRIBUTION ALONG TUBING

FEB 28 1996 - 2
SS-304L / 60°C to 40°C
HIGH %RH / MED [I₂]g

IODINE (mol/L) vs TIME (min)

IODINE DISTRIBUTION ALONG TUBING
60°C - HIGH %RH - LOW [I₂]g

JUNE 24, 96 - 1
SS-304L / 60°C
HIGH RH / LOW [I₂]g

IODINE DISTRIBUTION ALONG TUBING

[I₂]g mol/L

IODINE (mol/cm²)

0.0E+00
-5.0E-11
5.0E-11
-5.0E-11
5.0E-11
1.0E-10
1.5E-10
2.0E-10
2.5E-10
3.0E-10
3.5E-10
4.0E-10
4.5E-10
5.0E-10
0.0E+00
50 100 150 200 250 300
TIME (min)

iodine (mol/cm²)
- - [I₂]g mol/L

60°C - HIGH %RH - LOW [I₂]g

JUNE 24, 96 - 2
SS-304L / 60°C
HIGH %RH / LOW [I₂]g

IODINE DISTRIBUTION ALONG TUBING

[I₂]g mol/L

IODINE (mol/cm²)

0.0E+00
-1.0E-10
5.0E-11
1.0E-10
1.5E-10
2.0E-10
2.5E-10
3.0E-10
3.5E-10
4.0E-10
4.5E-10
5.0E-10
0.0E+00
50 100 150 200 250 300
TIME (min)

iodine (mol/cm²)
- - [I₂]g mol/L

IODINE (dpm)

0 2000 4000
0
0 5 10 15 20 25
cm FROM INLET

iodine (dpm)

0 2000 4000
0
0 5 10 15 20 25
cm FROM INLET
60°C - LOW %RH - MED [I₂]g

JULY 18, '96 - 2
SS-304L / 60°C
LOW %RH / MED [I₂]g

[IODINE] mol/cm²

TIME (min)

0 100 200 300 400

[IODINE] mol/L

-1.0E-10 -5.0E-11 0.0E+00 1.0E-10 5.0E-11 1.5E-10 2.0E-10 2.5E-10 3.0E-10

Iodine (mol/cm²)
[I₂]g mol/L

IODINE DISTRIBUTION ALONG TUBING

0 5 10 15 20 25

500 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500 7000 7500

cm FROM INLET

60°C - LOW %RH - MED [I₂]g

OCT 24, '96 - 1
SS-304L / 60°C
LOW RH / MED [I₂]g

[IODINE] mol/cm²

TIME (min)

0 50 100 150 200 250 300

[IODINE] mol/L

-1.0E-10 -5.0E-11 0.0E+00 1.0E-10 5.0E-11 1.5E-10 2.0E-10 2.5E-10 3.0E-10

Iodine (mol/cm²)
[I₂]g mol/L

IODINE DISTRIBUTION ALONG TUBING

0 5 10 15 20 25

0 500 1000 1500 2000 2500 3000 3500 4000 4500 5000 5500 6000 6500 7000 7500

cm FROM INLET
90°C - HIGH %RH - MED $[\textit{i}_2]g$

MAY 24, 96 - 1
SS-304L / 90°C HIGH %RH / MED $[\textit{i}_2]g$

IODINE DISTRIBUTION ALONG TUBING

IODINE (mol/cm²)

IODINE (mol/L)

IODINE (dpm)

cm FROM INLET

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)
90°C - HIGH %RH - MED [I₂]g

JUNE 17, 96 - 1

SS-304L / 90 C
HIGH %RH / MED [I₂]g

IODINE (mol/cm²)

0.0E+00 1.0E-10 2.0E-10 3.0E-10 4.0E-10 5.0E-10 6.0E-10

[I₂]g mol/L

0.0E+00 2.0E-10 4.0E-10 6.0E-10 8.0E-10 1.0E-09 1.2E-09 1.4E-09 1.6E-09 1.8E-09 2.0E-09

TIME (min)

0 50 100 150 200

IODINE DISTRIBUTION ALONG TUBING

IODINE (dpm)

0 2000 4000 6000 8000

0 5 10 15 20 25 cm FROM INLET
90°C - LOW %RH - MED $[I_2]g$

**JULY 17, 96 - 1**

**SS-304L / 90°C**

LOW %RH / MED $[I_2]g$

**IODINE DISTRIBUTION ALONG TUBING**

- Iodine (mol/cm$^2$)
- $[I_2]g$ mol/L

**IODINE (mol/cm$^2$)**

- 4.0E-10
- 3.0E-10
- 2.0E-10
- 1.0E-10
- 0.0E+00
- -1.0E-10
- -2.0E-10

**TIME (min)**

- 0
- 50
- 100
- 150
- 200
- 250
- 300

**IODINE (mol/cm²)**

- 4.0E-09
- 8.0E-09
- 1.2E-08
- 1.6E-08
- 2.0E-08

**IODINE (dpm)**

- 600
- 400
- 200
- 100
- 0

**cm FROM INLET**

- 0
- 5
- 10
- 15
- 20
- 25
Appendix B - Tabulated Results: Adsorption

Table B.1 SS-316L High [I₂]ₚ - High %RH

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>k_d (cm/s)</th>
<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Apr 27 95-1</td>
<td>3.6 x 10⁻⁷</td>
<td>23</td>
<td>2.7 x 10⁻⁴</td>
<td>1.04 x 10⁻¹⁶</td>
<td>10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>2 Mar 21 95-1</td>
<td>6.0 x 10⁻⁷</td>
<td>23</td>
<td>1.8 x 10⁻⁴</td>
<td>1.09 x 10⁻¹⁶</td>
<td>10⁻⁷ mol/cm²</td>
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<tr>
<td>3 May 4 95-1</td>
<td>5.5 x 10⁻⁷</td>
<td>23</td>
<td>2.9 x 10⁻⁴</td>
<td>1.6 x 10⁻¹⁶</td>
<td>10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>4 May 4 95-2</td>
<td>5.5 x 10⁻⁷</td>
<td>23</td>
<td>3.3 x 10⁻⁴</td>
<td>1.8 x 10⁻¹⁶</td>
<td>10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>5 May 9 96-1</td>
<td>1.8 x 10⁻⁷</td>
<td>40</td>
<td>1.6 x 10⁻⁴</td>
<td>3.0 x 10⁻¹⁶</td>
<td>&gt; 2 x 10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>6 May 9 96-2</td>
<td>1.8 x 10⁻⁷</td>
<td>40</td>
<td>2.2 x 10⁻⁴</td>
<td>3.9 x 10⁻¹⁶</td>
<td>&gt; 2 x 10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>7 May 8 96-1</td>
<td>1.8 x 10⁻⁷</td>
<td>60</td>
<td>1.4 x 10⁻⁴</td>
<td>3.6 x 10⁻¹⁶</td>
<td>&gt; 10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>8 May 8 96-2</td>
<td>1.8 x 10⁻⁷</td>
<td>60</td>
<td>2.1 x 10⁻⁴</td>
<td>3.7 x 10⁻¹⁶</td>
<td>&gt; 10⁻⁷ mol/cm²</td>
</tr>
<tr>
<td>9 Apr 19 96-2</td>
<td>4 x 10⁻⁷</td>
<td>90</td>
<td>2 x 10⁻⁵</td>
<td>8 x 10⁻¹⁴</td>
<td>&gt; 10⁻⁸ mol/cm²</td>
</tr>
</tbody>
</table>

Table B.2 SS-316L High [I₂]ₚ - Low %RH

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>k_d (cm/s)</th>
<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Jun 20 95-1</td>
<td>4.8 x 10⁻⁸</td>
<td>23</td>
<td>7 x 10⁻⁴</td>
<td>3.20 x 10⁻¹⁶</td>
<td>&gt; 10⁻⁶ mol/cm²</td>
</tr>
<tr>
<td>2 Jun 20 95-2</td>
<td>4.8 x 10⁻⁸</td>
<td>23</td>
<td>7 x 10⁻⁴</td>
<td>3.48 x 10⁻¹⁶</td>
<td>&gt; 10⁻⁶ mol/cm²</td>
</tr>
<tr>
<td>3 Jun 21 95-1</td>
<td>3.8 x 10⁻⁸</td>
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<td>1.06 x 10⁻¹⁶</td>
<td>&gt; 10⁻⁶ mol/cm²</td>
</tr>
<tr>
<td>4 Jun 21 95-2</td>
<td>3.8 x 10⁻⁸</td>
<td>23</td>
<td>3.2 x 10⁻⁴</td>
<td>1.22 x 10⁻¹⁶</td>
<td>&gt; 10⁻⁶ mol/cm²</td>
</tr>
<tr>
<td>5 Dec 20 96-1</td>
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<td>1.2 x 10⁻⁴</td>
<td>1.6 x 10⁻¹⁴</td>
<td>&gt; 3 x 10⁻¹⁷ mol/cm²</td>
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<tr>
<td>6 Dec 20 96-2</td>
<td>1.4 x 10⁻⁷</td>
<td>40</td>
<td>2.1 x 10⁻⁴</td>
<td>3.0 x 10⁻¹⁴</td>
<td>&gt; 5 x 10⁻¹⁷ mol/cm²</td>
</tr>
<tr>
<td>7 Dec 23 96-1</td>
<td>1.7 x 10⁻⁷</td>
<td>40</td>
<td>3.6 x 10⁻⁴</td>
<td>6.0 x 10⁻¹⁴</td>
<td>&gt; 4 x 10⁻¹⁷ mol/cm²</td>
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<tr>
<td>8 Dec 23 96-2</td>
<td>1.7 x 10⁻⁷</td>
<td>40</td>
<td>1.2 x 10⁻⁴</td>
<td>1.9 x 10⁻¹⁴</td>
<td>&gt; 3 x 10⁻¹⁷ mol/cm²</td>
</tr>
<tr>
<td>9 Apr 26 96-1</td>
<td>6 x 10⁻⁸</td>
<td>60</td>
<td>(3 x 10⁻⁷)*</td>
<td>(2 x 10⁻¹⁴)*</td>
<td>(&gt; 3 x 10⁻¹⁷ mol/cm²)*</td>
</tr>
<tr>
<td>10 Apr 26 96-2</td>
<td>6 x 10⁻⁸</td>
<td>60</td>
<td>(3 x 10⁻⁷)*</td>
<td>(2 x 10⁻¹⁴)*</td>
<td>(&gt; 3 x 10⁻¹⁷ mol/cm²)*</td>
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<tr>
<td>11 Jan 17 96-1</td>
<td>9 x 10⁻⁸</td>
<td>90</td>
<td>1.1 x 10⁻⁵</td>
<td>9.5 x 10⁻¹⁴</td>
<td>&gt; 1.4 x 10⁻⁷ mol/cm²</td>
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</tbody>
</table>
Table B.3 SS-304L High $[I_2]_g$ - High %RH

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Deposition rate (mol/cm$^2$.s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jun 1 95 - 1</td>
<td>5 x10$^{-7}$</td>
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<td>1.4 x10$^{-5}$</td>
<td>6.9 x10$^{-15}$</td>
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<td>5x10$^{-8}$ mol/cm$^2$</td>
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<td>May 3 96 - 1</td>
<td>3.5 x10$^{-7}$</td>
<td>40</td>
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<td>1.43 x10$^{-10}$</td>
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<td></td>
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<td>&gt; 5x10$^{-7}$ mol/cm$^2$</td>
</tr>
<tr>
<td>3</td>
<td>May 3 96 - 2</td>
<td>3.5 x10$^{-7}$</td>
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<td>3.7 x10$^{-4}$</td>
<td>1.28 x10$^{-10}$</td>
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<td>&gt; 4x10$^{-7}$ mol/cm$^2$</td>
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<td>&gt; 10$^{-6}$ mol/cm$^2$</td>
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<tr>
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<td>Apr 22 96 - 2</td>
<td>4.0 x10$^{-7}$</td>
<td>60</td>
<td>3.0 x10$^{-4}$</td>
<td>1.22 x10$^{-10}$</td>
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<tr>
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<td>Apr 21 96 - 1</td>
<td>3 x10$^{-7}$</td>
<td>90</td>
<td>6 x10$^{-7}$</td>
<td>1.9 x10$^{-11}$</td>
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</tr>
<tr>
<td>7</td>
<td>Apr 21 96 - 2</td>
<td>3 x10$^{-7}$</td>
<td>90</td>
<td>5 x10$^{-7}$</td>
<td>1.5 x10$^{-11}$</td>
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</table>

Table B.4 SS-304L High $[I_2]_g$ - Low %RH

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<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Deposition rate (mol/cm$^2$.s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jan 26 96 - 1</td>
<td>2 x10$^{-8}$</td>
<td>23</td>
<td>5 x10$^{-5}$</td>
<td>10$^{-15}$</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>&gt; 1.5x10$^{-9}$ mol/cm$^2$</td>
</tr>
<tr>
<td>2</td>
<td>Jan 30 96 - 1</td>
<td>6.5 x10$^{-8}$</td>
<td>23</td>
<td>2 x10$^{-5}$</td>
<td>10$^{-15}$</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt; 2x10$^{-9}$ mol/cm$^2$</td>
</tr>
<tr>
<td>3</td>
<td>Aug 27 96 - 1</td>
<td>9 x10$^{-8}$</td>
<td>40</td>
<td>1.9 x10$^{-7}$</td>
<td>1.7x10$^{-13}$</td>
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<td>5x10$^{-9}$ mol/cm$^2$</td>
</tr>
<tr>
<td>4</td>
<td>Aug 23 96 - 1</td>
<td>9 x10$^{-8}$</td>
<td>60</td>
<td>1.8 x10$^{-7}$</td>
<td>1.65x10$^{-13}$</td>
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</tr>
<tr>
<td>5</td>
<td>Aug 23 96 - 2</td>
<td>9 x10$^{-8}$</td>
<td>60</td>
<td>2.3 x10$^{-7}$</td>
<td>2.11x10$^{-13}$</td>
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<td>&gt; 2.5x10$^{-9}$ mol/cm$^2$</td>
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<tr>
<td>6</td>
<td>Jul 11 96 - 1</td>
<td>8.0 x10$^{-8}$</td>
<td>90</td>
<td>2.6 x10$^{-7}$</td>
<td>2.1x10$^{-12}$</td>
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<td>2x10$^{-9}$ mol/cm$^2$</td>
</tr>
<tr>
<td>7</td>
<td>Jul 11 96 - 2</td>
<td>8.0 x10$^{-8}$</td>
<td>90</td>
<td>1.8 x10$^{-7}$</td>
<td>1.5 x10$^{-12}$</td>
</tr>
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<td></td>
<td>2x10$^{-9}$ mol/cm$^2$</td>
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</table>
Table B.5 SS-316L Medium $[I_2]_g$ - High %RH

<table>
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<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jul 7 95 - 1</td>
<td>23</td>
<td>$1.3 \times 10^{-2}$</td>
<td>1.8E-13</td>
<td>&gt; $6.5 \times 10^{-7}$ mol/cm²</td>
</tr>
<tr>
<td>2</td>
<td>Jul 10 95 - 1</td>
<td>23</td>
<td>$3.5 \times 10^{-1}$</td>
<td>8.3 $\times 10^{-12}$</td>
<td>$4 \times 10^{-8}$ mol/cm²</td>
</tr>
<tr>
<td>3</td>
<td>Jul 21 95 - 1</td>
<td>23</td>
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<td>9.30 $\times 10^{-12}$</td>
<td>1.6 $\times 10^{-7}$ mol/cm²</td>
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<td>23</td>
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<td>5.40 $\times 10^{-12}$</td>
<td>1.4 $\times 10^{-7}$ mol/cm²</td>
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<td>3.0E-13</td>
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</tr>
<tr>
<td>7</td>
<td>Feb 13 96 - 1</td>
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<td>$2.2 \times 10^{-1}$</td>
<td>2.43 $\times 10^{-12}$</td>
<td>1.6 $\times 10^{-7}$ mol/cm²</td>
</tr>
<tr>
<td>8</td>
<td>Sep 10 96 - 1</td>
<td>40</td>
<td>$3.8 \times 10^{-1}$</td>
<td>9.69 $\times 10^{-12}$</td>
<td>&gt; 4.5 $\times 10^{-7}$ mol/cm²</td>
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<td>Sep 10 96 - 2</td>
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<td>$1.7 \times 10^{-1}$</td>
<td>4.34 $\times 10^{-12}$</td>
<td>&gt; 2.4 $\times 10^{-7}$ mol/cm²</td>
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<td>$1.2 \times 10^{-1}$</td>
<td>1.54 $\times 10^{-12}$</td>
<td>&gt; 1.6 $\times 10^{-8}$ mol/cm²</td>
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<tr>
<td>11</td>
<td>Jul 22 96 - 2</td>
<td>60</td>
<td>$8 \times 10^{-7}$</td>
<td>1 $\times 10^{-12}$</td>
<td>&gt; 8 $\times 10^{-13}$ mol/cm²</td>
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<tr>
<td>12</td>
<td>May 23 96 - 1</td>
<td>90</td>
<td>(3 $\times 10^{-5})$*</td>
<td>(2 $\times 10^{-15})$*</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>May 23 96 - 2</td>
<td>90</td>
<td>(7 $\times 10^{-5})$*</td>
<td>(4 $\times 10^{-14})$*</td>
<td>-</td>
</tr>
</tbody>
</table>

Table B.6 SS-316L Medium $[I_2]_g$ - Low %RH

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jul 7 95 - 1</td>
<td>23</td>
<td>$4 \times 10^{-2}$</td>
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<td>&gt; 4 $\times 10^{-10}$ mol/cm²</td>
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<tr>
<td>2</td>
<td>Jul 10 95 - 1</td>
<td>23</td>
<td>$2.3 \times 10^{-2}$</td>
<td>4.9 $\times 10^{-14}$</td>
<td>&gt; 3 $\times 10^{-10}$ mol/cm²</td>
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<td>3</td>
<td>Feb 13 96 - 1</td>
<td>40</td>
<td>$5 \times 10^{-2}$</td>
<td>1.6 $\times 10^{-14}$</td>
<td>&gt; 8 $\times 10^{-11}$ mol/cm²</td>
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<td>4</td>
<td>Sep 10 96 - 1</td>
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<td>$2 \times 10^{-2}$</td>
<td>6.7 $\times 10^{-14}$</td>
<td>&gt; 8 $\times 10^{-10}$ mol/cm²</td>
</tr>
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<td>&gt; 2 $\times 10^{-10}$ mol/cm²</td>
</tr>
<tr>
<td>6</td>
<td>Oct 30 96 - 1</td>
<td>60</td>
<td>$1.2 \times 10^{-3}$</td>
<td>3.8 $\times 10^{-13}$</td>
<td>1 $\times 10^{-10}$ mol/cm²</td>
</tr>
<tr>
<td>7</td>
<td>Oct 30 96 - 2</td>
<td>60</td>
<td>$2.6 \times 10^{-2}$</td>
<td>5.2 $\times 10^{-13}$</td>
<td>1.4 $\times 10^{-10}$ mol/cm²</td>
</tr>
<tr>
<td>8</td>
<td>May 20 96 - 1</td>
<td>90</td>
<td>(6 $\times 10^{-7})$*</td>
<td>(2 $\times 10^{-15})$*</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>May 20 96 - 2</td>
<td>90</td>
<td>$1 \times 10^{-2}$</td>
<td>3 $\times 10^{-15}$</td>
<td>&gt; 1 $\times 10^{-13}$ mol/cm²</td>
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</tbody>
</table>
Table B.7 SS-304L Medium $[I_2]_g$ - High %RH

<table>
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<tr>
<th>Experiment</th>
<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Apr 30 96-1</td>
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<td>(1 x 10⁻²)</td>
<td>(3 x 10⁻¹⁷)</td>
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<td>Apr 30 96-2</td>
<td>2.6 x 10⁻⁸</td>
<td>23</td>
<td>(2 x 10⁻²)</td>
<td>(5 x 10⁻¹⁷)</td>
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<tr>
<td>3</td>
<td>Feb 28 96-1</td>
<td>4.0 x 10⁻⁸</td>
<td>40</td>
<td>5 x 10⁻²</td>
<td>1.8 x 10⁻¹⁴</td>
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<td>1.7 x 10⁻²</td>
<td>6.7 x 10⁻¹⁴</td>
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<td>1.5 x 10⁻¹⁴</td>
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<td>4 x 10⁻³</td>
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<td>(7 x 10⁻²)*</td>
<td>(2 x 10⁻¹⁵)*</td>
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Table B.8 SS-304L Medium $[I_2]_g$ - Low %RH

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<th>Gas Phase (mol/L)</th>
<th>Temp (°C)</th>
<th>$k_d$ (cm/s)</th>
<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
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<tr>
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Table B.9 SS-316L Low \([I_2]_g\) - High %RH

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<th>Deposition rate (mol/cm².s)</th>
<th>Maximum Loading</th>
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<td>23</td>
<td>(9 \times 10^{-7})*</td>
<td>(2 \times 10^{-15})*</td>
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<tr>
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<td>Mar 29 96 - 1</td>
<td>2.9 \times 10^{-11}</td>
<td>40</td>
<td>(7 \times 10^{-7})*</td>
<td>(2 \times 10^{-15})*</td>
</tr>
<tr>
<td>3</td>
<td>Mar 29 96 - 2</td>
<td>2.9 \times 10^{-11}</td>
<td>40</td>
<td>(7 \times 10^{-7})*</td>
<td>(2 \times 10^{-15})*</td>
</tr>
<tr>
<td>4</td>
<td>Jul 4 96 - 2</td>
<td>2.1 \times 10^{-11}</td>
<td>40</td>
<td>(9 \times 10^{-7})*</td>
<td>(2 \times 10^{-18})*</td>
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<tr>
<td>5</td>
<td>Mar 25 96 - 1</td>
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<td>60</td>
<td>(5 \times 10^{-7})*</td>
<td>(2 \times 10^{-18})*</td>
</tr>
<tr>
<td>6</td>
<td>Mar 25 96 - 2</td>
<td>4.0 \times 10^{-11}</td>
<td>60</td>
<td>(5 \times 10^{-7})*</td>
<td>(2 \times 10^{-18})*</td>
</tr>
<tr>
<td>7</td>
<td>Jul 2 96 - 1</td>
<td>2.5 \times 10^{-10}</td>
<td>60</td>
<td>(8 \times 10^{-7})*</td>
<td>(2 \times 10^{-14})*</td>
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<td>90</td>
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<td>(6 \times 10^{-18})*</td>
</tr>
<tr>
<td>9</td>
<td>Mar 21 96 - 2</td>
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<td>90</td>
<td>(1 \times 10^{-7})*</td>
<td>(6 \times 10^{-18})*</td>
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<td>90</td>
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<td>(2 \times 10^{-15})*</td>
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<td>Gas Phase (mol/L)</td>
<td>Temp (°C)</td>
<td>$k_d$ (cm/s)</td>
<td>Deposition rate (mol/cm².s)</td>
<td>Maximum Loading</td>
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<td>-------------------</td>
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<td>--------------</td>
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<tr>
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<td>23</td>
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<tr>
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<td>$(1 \times 10^{-15})^*$</td>
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<tr>
<td>Nov 9 96 - 2</td>
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<td>23</td>
<td>$2 \times 10^{-1}$</td>
<td>$4 \times 10^{-14}$</td>
<td>$6 \times 10^{-11}$ mol/cm²</td>
</tr>
<tr>
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<td>$(2 \times 10^{-16})^*$</td>
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<tr>
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<td>$(1 \times 10^{-15})^*$</td>
<td>-</td>
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<tr>
<td>Mar 25 96 - 2</td>
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<td>60</td>
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<td>$(1 \times 10^{-15})^*$</td>
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<td>$(2 \times 10^{-15})^*$</td>
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<td>$(5 \times 10^{-16})^*$</td>
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<td>90</td>
<td>$(2 \times 10^{-2})^*$</td>
<td>$(5 \times 10^{-16})^*$</td>
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<tr>
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### Table B.11 SS-304L Low [I₂]₉ - High %RH

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<th>Temp (°C)</th>
<th>kₐ (cm/s)</th>
<th>Deposition rate (mol/cm²·s)</th>
<th>Maximum Loading</th>
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<td>23</td>
<td>(6 x 10⁻²)</td>
<td>(9 x 10⁻¹⁵)</td>
</tr>
<tr>
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<td>7.6 x 10⁻¹⁷</td>
<td>23</td>
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<td>1.7 x 10⁻¹⁴</td>
</tr>
<tr>
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<td>7.6 x 10⁻¹⁷</td>
<td>23</td>
<td>6 x 10⁻²</td>
<td>4.2 x 10⁻¹⁴</td>
</tr>
<tr>
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<td>Jun 25 96 - 1</td>
<td>2.5 x 10⁻¹⁷</td>
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<td>4.4 x 10⁻¹⁴</td>
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### Table B.12 SS-304L Low [I₂]₉ - Low %RH

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<th>kₐ (cm/s)</th>
<th>Deposition rate (mol/cm²·s)</th>
<th>Maximum Loading</th>
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</tr>
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<td>Jun 18 96 - 2</td>
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<td>Nov 6 96 - 2</td>
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<td>4.4 x 10⁻¹⁴</td>
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### Table B.1 Desorption results

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<td>23°C / High RH</td>
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<td>23°C / High RH</td>
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<td>90°C / High RH</td>
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<td>60°C / High RH</td>
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<td>60°C / High RH</td>
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<td>90°C / Low RH / High I$_2$</td>
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Appendix D - Classifications of Operating Variables and Reproducibility of Results

D.1 Gas Phase Concentration

As described in table 5.1, iodine concentration was divided into three different categories. One problem that was difficult to resolve was control of fluctuations in the gas concentration during an experiment. Generally, the trend was a declining gas concentration with time. This drop was mainly due to the limitation in the method for gaseous iodine generation as described in the experimental chapter.

A substantial drop was observed especially in experiments at high and medium gas concentration. In some cases, the final concentration was only 35% of the initial value. Less severe decrease was observed for experiments at low concentration. Between the beginning and the end of such experiments, the concentration declined by 10% to 30%. Regardless of this fluctuation, all concentrations were still kept within the proper range of iodine concentration as intended for the corresponding experiment. For the purpose of calculating $k_d$, the average value observed during the initial period was used.

D.2 Tube Surface Temperature and Relative Humidity

There was no significant problem in the control of tube surface temperature. Maximum fluctuation for the tube surface temperature was $\pm 3^\circ C$ from the set point value. The relative humidity, however, followed different trends at low and high humidity. At high humidity the water content of the gas stream decreased with time as the amount of water in the bubbler was depleted. The reduction in relative humidity could be up to 10%. As in the
case of iodine gas concentration. despite this declining relative humidity, the obtained values were still within the desired range.

During dry experiments, the humidity was more stable. This was mainly due to the effectiveness of the dehumidification system. The only limitation was caused by the humidity brought by the gas stream that carried the iodine. Based on the downstream RH probe, the iodine source typically increased the humidity to less than 15%. In all the dry experiments, the range of relative humidity was between 0% and 25%. Questions arose as to whether the behavior of iodine deposition would be consistent within this wide range. An experiment was carried out to see the effect of increasing relative humidity within this range.

The experiment was performed at 60°C and medium gas phase concentration. The relative humidity was initially set near 0%. When the iodine loading was at maximum, the relative humidity was increased incrementally until a value of 30% was reached. The results showed that at this low surface loading no observable change in the behavior of iodine deposition occurred (figure D.1).
Figure D.1 Iodine deposition at low humidity (0% to 30%)

A similar test was also carried out at 60°C and high iodine gas phase concentration. The purpose of these experiments was to observe the difference in iodine deposition behavior under different ranges of relative humidity. In this test, the humidity was initially maintained less than 25%. Approximately 6 hours into the experiment, the relative humidity was increased to 50% and a sudden substantial increase in the rate of iodine deposition occurred (figure D.2). The rate of deposition was similar to that observed at high relative humidity.
This experiment indicates that deposition behavior at medium humidity should be similar to that at high humidity. A similar trend was reported by Deir\textsuperscript{1}. The data also supports the role of water in increasing the rate of iodine deposition on stainless steel.

**D.3 Reproducibility of Results**

The apparatus being used in the study allowed simultaneous testing of two tubing samples so that for most experiments, duplicated results were obtained. Some problems were encountered with one of the NaI detectors preventing duplications for a few of experiments. In such cases, additional experiment under similar operating conditions were carried out.

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Even when simultaneous measurements were obtained, some additional runs were still performed to ensure that the observed trend of deposition was reproducible. This was required especially for experiments at low gas concentrations in which variations in results were observed. Iodine deposition at low gas concentrations was generally lower than deposition at higher concentrations. This made it difficult to obtain a reading that was free from fluctuation due to background interference. One partial solution to the problem was the use of higher specific activity by adding a larger amount of $^{131}$I tracer. There was, however, a limit to the amount of tracer that could be used in a single experiment for safety considerations. Consequently, for some low concentration experiments, considerable uncertainty was associated with the readings. In the tabulation of results, the uncertainty is reflected in the last significant digit. For cases involving very low iodine deposition, such that the reading was mostly due to background variation the values reported are based on the detection limit. Another problem that was encountered was the inhomogeneity of the material. Some variations in results were expected due to this inhomogeneity.

Despite all the variations described above, the replicates to measurements of deposition velocity generally fluctuated around approximately 20% of the average value (see appendix B). This variation was less than the effect of changing operating conditions, hence it did not prevent the recognition of the general trends in the experimental parameters under investigation. Moreover, as mentioned earlier, some experiments were repeated to ensure that the observed trends could be correctly attributed to the effects of the operating conditions. Conservative measures should be taken when estimating iodine losses in the sampling lines
to avoid underestimating the loss. Recommended values of deposition parameters are listed in table 5.6.

The following figure shows results from two performed at 40°C and high iodine concentration but with different relative humidity. As can be seen, in spite of any variations due to limitation in the method and apparatus, the different trends of deposition under various operating conditions could still be recognized. This is especially true for experiment under high gas phase concentration.

![Iodine Surface Concentration Vs Time (SS-316L)](image)

**Figure D.3** Iodine deposition under different relative humidities