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Investigation of Iron in High Temperature Molten Liquid Lead Using the Lennard-Jones Potential

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Abstract. Liquid metal corrosion is getting more attentions by nuclear material researchers. The information about corrosions and damages mechanism of nuclear structural materials are very important for nuclear reactor design. In this current work we study the corrosion of iron when immersed in liquid lead. We study the phenomena by molecular dynamics method based on the Lennard-Jones potential for interaction between two neutral atoms the material. The potential has two parameters i.e. collision parameter(σ) and energy (ε). We also study the iron corrosion inhibition by using nitrogen agent. To simulate the corrosion phenomena, we use the MOLDY molecular dynamics program. For doing this we need to verify the used Lennard-Jones potential parameters firstly. The verification is done by adjusting the two parameters (σ, ε till the value of diffusion coefficient (iron in liquid lead) is similar between simulation and experiment, under certain small error. The two parameters (σ, ε in this work after some correction should be the best value for studying corrosion inhibition or others. We got new parameter $\varepsilon = 0.4007eV$ and$\sigma = 2.3894$Å for iron, while for lead $\varepsilon = 0.1910eV$and $\sigma = 2.9578$Å. By using these parameters in simulation of corrosion inhibition using nitrogen, we can make estimation that for reducing the iron corrosion, it is recommended if we inject nitrogen gas into liquid lead for about concentration of $0.29wt\%$for the best inhibition.

THEORETICAL BACKGROUND

Technological development has increasingly facilitated human work with variety of methods to produce energy. One effective way to produce large amount of energy is the use of nuclear power plant. Nowadays one of the promising candidates is using the fast nuclear reactor type that uses liquid metal (as lead) for supporting the cooling system. This reactor has advantages for future development of nuclear reactor however it was still known showing crucial problem in applications. There is a severe corrosion of structural materials (as steels) when it interacts with liquid metal coolant. This interaction causes the diffusion of components of steels into liquid metal, as iron, chromium, etc [1]. We need a special effort to overcome this high corrosion by finding better new materials or method of reducing corrosion.

Liquid lead metal corrosion is a special corrosion called "hot corrosion" and in this case we can study the corrosion based on the diffusion process where the diffusion coefficient calculation is important [2]. The diffusion coefficient is a physical quantity that shows the ability of a material to diffuse at a concentration gradient. This amount depends on the composition of atoms in the material and the nature of other substances that can spread. The diffusion coefficient can be determined through the experimental method, as in Table 1 as follows :

TABLE 1. Diffusion coefficient is based on experiments

Elements	$D(T)$ [m^2/s]
Iron [4]	$D(2000K) = 1.557x10^{-10}$
Lead [5]	$D(743K) = 2.427x10^{-9}$

Unfortunately, there is no complete data of diffusion for all elements from experimental measurements, especially for high temperature condition.

Diffusion coefficient can also be determined by computer simulation, as molecular dynamics simulation [6]. Simulation using (classical) molecular dynamics method requires a specific potential function that describes the atomic interactions of atoms in material. One of potentials that simple but very popular i.e. the Lennard-Jones potential. The Lennard-Jones potential is a potential that uses a mathematical approach to describe the interaction energy between two atoms or nonbonding molecules based on the separation distance. This potential

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has only two parameters, namely the parameters of distance (σ) and energy (ε). The potential parameters of Lennard-Jones are often obtained based on experimental measurement data such as material viscosity [7]. Table 2 shows Lennard-Jones potential parameters of iron and lead.

TABLE 2. Lennard-Jones potential parameters[3]

pair interaction	$\varepsilon(eV)$	$\sigma(\text{Å})$
$Fe-Fe$	0.4007	2.3193
$Pb-Pb$	0.1910	3.1888
$N-N$	0.0085	3.6560

While for cross interaction, namely Fe-Pb, Fe-N, Pb-N, the well-known formula is used, namely the Lorentz-Berthelot formula:

$$\sigma_{ab} = \frac{(\sigma_{aa}+\sigma_{bb})}{2} \quad (1)$$

$$\varepsilon_{ab} = \sqrt{\varepsilon_{aa} \times \varepsilon_{bb}} \quad (2)$$

σ_{ab} means the collision parameter between two different atoms A and B. ε_{ab} means the depth of potential energy between two different atoms A and B. A simple form of Lennard-Jones potential to describe the interaction between two neutral atoms/molecules can be written as follows:

$$U(r) = 4\left\{\left(\frac{}{r}\right)^{12} - \left(\frac{}{r}\right)^{6}\right\} \quad (3)$$

In this equation, the $U(r)$ is the potential of two atoms, and r is the separation between two atoms. In this current work we use the Lennard-Jones potential for simulating the corrosion phenomena and its inhibition. We use the MOLDY molecular dynamics program to do all simulations. In the mean time the Lennard-Jones potential is so simple that may not so suitable for metal system. So for the first procedure later is to find the best potential parameters (σ,ε) for simulation when we use MOLDY..

The (self-)diffusion coefficient can be known from molecular dynamics simulation and calculated by using various formulations as Einstein relation. The Einstein relation is a theory that studying atomic properties and molecular kinematics where the value of the diffusion coefficient is obtained through the slope of the MSD (Mean Square Displacement) curve with time,

$$MSD = \left(r_i(t) - r_i(0)\right)^2 \quad (4)$$

$$D = \frac{1}{6t} MSD \quad (5)$$

The D is the diffusion coefficient and t is a time so from Equation (5) we can see that the diffusion coefficient d is the slope of the graph of MSD vs. time. Using this formulation, simulations can be made to study the physical processes that occur microscopically[8]. In the corrosion process we will represent a steel with pure iron material and put it into molten liquid lead metal. If the corrosion occurs, then we will see high solubility of iron into liquid lead metal. To do this we will use the Moldy molecular dynamics software [6]. MOLDY is a computer program that can handle set of atoms of material as solids, liquid or gas. To visualize the corrosion, we will use Ovito program [9]. OVITO is one of the programs used for visualizing and analyzing the results of molecular dynamics simulation. The program is a standard visualization program with many advantages in terms of visualization including molecular structure and crystal structure, and in analytical facilities for simulation results.

The diffusion process is also effected by temperature. The temperature dependence diffusion coefficient $D(T)$ can be determined by Arrhenius formula:

$$D(T) = D_0 exp\left(\frac{-Q}{RT}\right)[\text{m}^2/\text{s}]. \quad (6)$$

where$D_0$is diffusion coefficient at nol kelvin, Q is activation energy to drive diffusion process, T is temperature and R is universal gas constant. By assuming that diffusion has linear relation to the temperature then we can determine D_0 and Q from equation:

$$lnD(T) = lnD_0 - \frac{Q}{RT} \tag{7}$$

We can determine the D_0 and Q by plotting this linear graph between $1/T$ and ln$D$ for many pair values.

METHOD

To investigate the corrosion of iron and it's inhibition, the simulation work is carried out in three stages:

1) Finding the best Lennard-Jones potential parameters (σ,ε) of material
2) Computing the diffusion coefficient of iron
3) Finding the best way of inhibiting the corrosion

Stage 1 & 2:

To study the corrosion, we need an appropriate potential parameter (σ, ε) of material system. We need to check this for simulation in Moldy code. For the first simulation we can use an available potential parameter as in Table 2 (we call old parameter). To find the best potential parameter, then we can do simulation for specific ensamble and control of simulation (especially for certain temperature), then compute the diffusion coefficient then compare the result (D^{sim}) and experimental result (D^{exp}), as in Table 1. We can set-up the (new) potential parameter (σ, ε) by adjusting this values for several simulation and re-compute the diffusion coefficient, till the discrepancy D^{sim} and D^{exp}, $|\Delta D|$is lower then 1%, where:

$$|\Delta D| = \frac{Dsimulation - Dexperiment}{Dexperiment} x100\% \tag{8}$$

Stage 3:

When we have gotten the best potential parameter (σ, ε) of material (iron and lead) then we continue the simulation for corrosion study. We put iron (bcc crystal 14x14x14 unit cell) into and in the center of liquid lead. The temperature of liquid lead is 1023K. We observed the structure stability of iron during simulation if is there any high corrosion? The corrosion can be shown by calculating the diffusion coefficient of Fe in liquid Pb. The greaterthe corrosion the bigger the diffusion coefficient D of Fe. The corrosion then will be reduced by injecting nitrogen at appropriate consentration into liquid lead. We have to find the best concentration for maximum reduction. The concentration of nitrogen in wt% in liquid lead can be computed by:

$$wt\% = \frac{(mxn)_{nitrogen}}{(mxn)_{nitrogen} + (mxn)_{lead}} \tag{9}$$

where:

m : mass of atom

n : number of atom

wt% : weight percent

RESULTS AND DISCUSSION

Determining the Best Lennard-Jones Potential Parameter of Iron

The simulation of iron diffusion coefficient D using old parameter had produced relatively significant different compared with experimental data. Then we try to find new parameter in which may produce the best parameter that causing smaller discrepancy ΔD. Table 3 is summary of the diffusion coefficients analysis.

TABLE 3. Comparison of old and new LJ parameters. $D_{2000}^{exp} = 1.557 \times 10^{-10}\ m^2/s$[4]

	ε	σ	D_{2000}^{sim}	$D(\%)$
Old	0.4007	2.3193	2.91531×10^{-10}	87.22
new	0.4007	2.3894	1.59069×10^{-10}	2.16

Using new LJ parameter then we can determine the temperature-dependent self diffusion coefficient $D(T)$. We evaluate the simulation in the range of $2000 - 5000K$, calculate the diffusion coefficient D and using to Equation 5 to btain Figure 1.

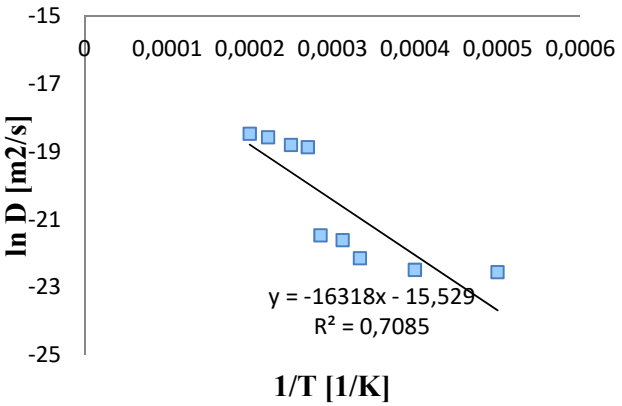

FIGURE 1. Graph of $1/T$ and lnD for iron

Figure 1 shows the plot of two variables (ln D vs $1/T$) following Eq. (7). The best R^2 value of this graph is 0.7085. Further analysis of Fig.1 we get: (T) :

$$D(T) = 1{,}9069x10^{-7} exp\left(\frac{-135766}{RT}\right) \tag{10}$$

Plotting Eq.(10) for several temperatures we get Fig.2 as below. :

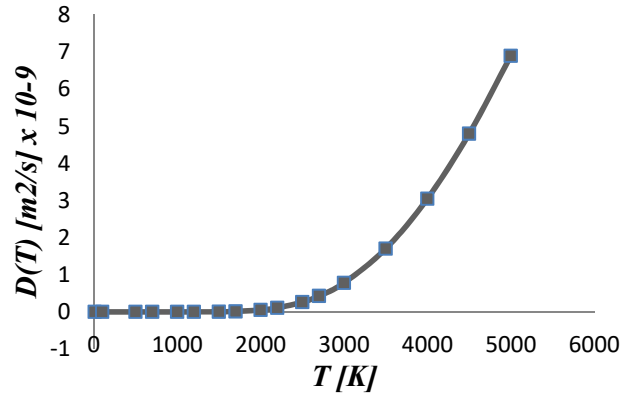

FIGURE 2. Graph of T and $D(T)$ for iron

We can see from Fig.2 that the difussion coefficient of iron starts to increase significantly after temperature about 2000 K.

Determining the Best Lennard-Jones Potential Parameter of Lead

The simulation of lead diffusion coefficient *D* using old parameter had produced relatively significant different compared with experimental data. As for lead, the results obtained are :

TABLE 4. Comparison of old and new LJ parameters. $D_{743}^{exp} = 2.427 \times 10^{-9}\, m^2/s$[5]

	ε	σ	D_{743}^{sim}	$D(\%)$
Old	0.1910	3.1888	1.1029×10^{-10}	95.46
new	0.1910	2.9578	2.408×10^{-9}	0.78

This parameter will be used to calculate the temperature diffusion coefficient of lead according to the Arrhenius formulation$D(T)$. The calculation is done by means of potential parameters that have been verified simulated with temperatures between $500 - 2000K$. Based on these simulations a variety of diffusion coefficient values are generated and then ploting the relationship simulation data between$1/T$and$lnD$to get the equation $D(T)$ as in the following graph:

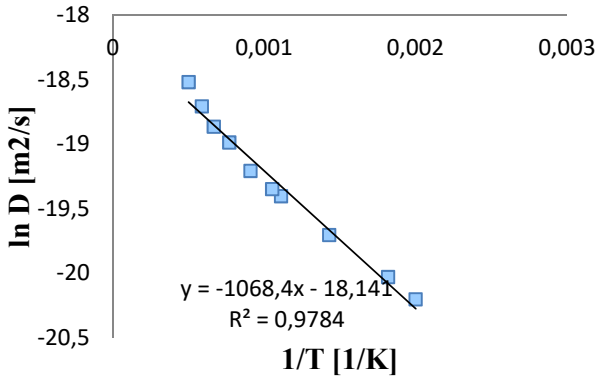

FIGURE 3. Graph of $1/T$andlnDin lead simulation

The Figure 3 shows that the simulation of lead resulting better graph with R^2 = 0.9784. Based on the results of the data fitting in the graph above, the equation of the self diffusion coefficient obtained for temperature for lead material is obtained:

$$D(T) = 1{,}399x10^{-8} exp\left(\frac{-8885{,}76}{RT}\right) \quad (11)$$

The following is a graph of the self diffusion coefficient of lead:

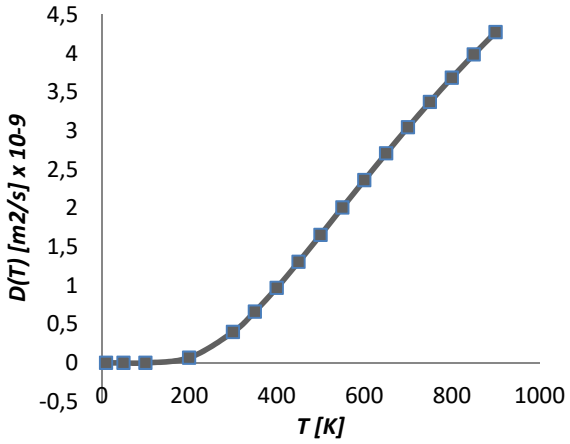

FIGURE 4. Graph of$T$and$D\left(T\right)$in lead simulation

Corrosion of Iron in Liquid Lead

The corrosion describes the damage of surface of ferrous metals in liquid lead. From the simulations, carried out for iron placed in liquid lead at a temperature of $1023K$, the resulting diffusion coefficient shows a tendency that an increase in temperature can increase the value of the diffusion coefficient which means that with changes in temperature the system can increase the diffusion rate of iron corrosion. Table 5 is the summary of the best LJ parameters after verification (correction).

TABLE 5. Lennard-Jones potential parameters verified

Interactions	$\varepsilon(eV)$	$\sigma(\text{Å})$
$Fe-Fe$	0.4007	2.3193
$Pb-Pb$	0.1910	3.1888
$N-N$[3]	0.0085	3.6560
$Fe-Pb$	0.2766	2.6736
$Pb-N$	0.0402	3.3069
$Fe-N$	0.0583	3.0227

Using the above parameters obtained the value of the diffusion coefficient is to$D(1023K) = 1{,}906x10^{-8}$]. Corrosion that occurs in iron in liquid lead can be inhibited by the addition of nitrogen gas. This nitrogen gas is injected into iron which is corroded with a certain concentration. Simulation is done by modeling iron in liquid lead with a potential parameter value that has been verified and also added nitrogen with a concentration between 0.05 - 0.33 wt%, it appears that there is an ideal potential for corrosion inhibition. As in the following Fig.5 :

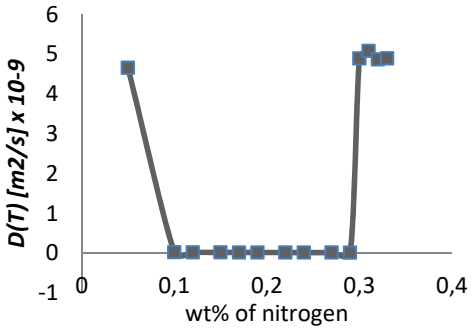

FIGURE 5. Graph of nitrogen addition, 0.05 wt% - 0.33 wt%

The picture above is a graph of the relationship of the concentration of nitrogen $(wt\%)$ with the value of the diffusion coefficient of iron produced $D(T)$.In the figure it can be seen that at a nitrogen concentration between $0.1 - 0.29wt\%$ the value of the iron diffusion coefficient is small. This indicates corrosion inhibition with the addition of nitrogen. If the percentage of nitrogen concentration is enlarged to $0.29wt\%$,it can be illustrated in the following Fi. 6 :

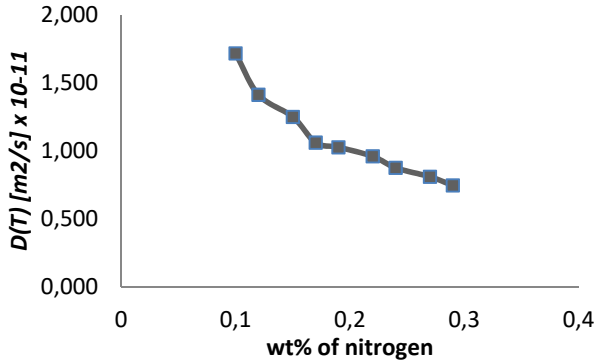

FIGURE 6.Graph of nitrogen addition nitrogen 0,1 wt% - 0,29 wt% with$D(T)$

In the simulation chart of corrosion inhibition with the addition of nitrogen gas at a temperature of $1023K$, the results show that when given nitrogen with a concentration $of 0.1wt\%$,the diffusion coefficient value of iron get smaller. The diffusion coefficient of iron before injecting nitrogen at temperature of $1023K$ is equal to$4.5172x10^{-9}\,m^2/s$,while when injected with a concentration of $0.1wt\%$ the diffusion coefficient value is equal to$1.7161x10^{-11}\,m^2/s$.The diffusion coefficient decreases until the level of $0.29wt\%$ is obtained by the value of the diffusion coefficient$7.4553x10^{-12}\,m^2/s$. However, the diffusion coefficient value rises again when the nitrogen concentration is added to exceed $0.3wt\%$, so it can be concluded that the best nitrogen concentration is $0.29wt\%$ indicated by the smallest diffusion coefficient value. This indicates that the structure of iron BCC is quite stable and its corrosion can be minimized when given a nitrogen concentration of $0.29wt\%$.

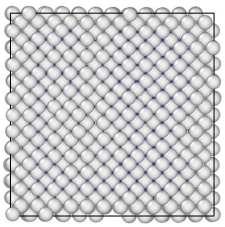

FIGURE 7. Iron before corrosion (before simulation)

The structure of iron crystal is BCC crystal before simulation (without liquid lead) as Fig.7. After we simulate the iron in liquid lead, then the iron experience high corrosion (no periodic structure) as in Fig.8.

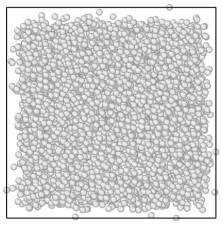

FIGURE 8. Iron corrosion at $T = 1023K$ (after simulation)

If we inject the oxygen at 0.05 wt% then the corrosion can be reduced. The structure of iron seems in periodic structure as Fig.9.

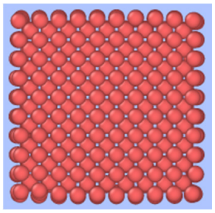

FIGURE 9. Iron corrosion at $T = 1023K$ with injection of nitrogen 0.05 wt%

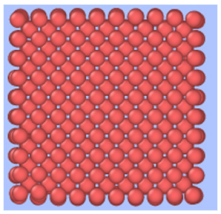

FIGURE 10. Iron corrosion at $T = 1023K$ with injection of nitrogen 0.29 wt%

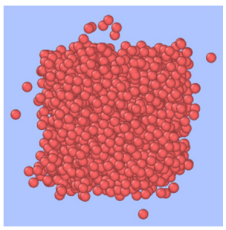

FIGURE 11. Iron corrosion at $T = 1023K$ with injection of nitrogen 0.3 wt%

However, if we put more nitrogen then the structure of iron starts to corrode as Fig.11.

From Fig.7 – 11 we can see that there is a significant difference between iron before corrosion and when corrosion occurs, where the iron crystal structure that has not been corroded is more regular than when corrosion. The structure of iron when injected 0.29 wt% nitrogen, shows more regular arragement compared to the injection of 0.05 wt% nitrogen. But when the concentration of nitrogen was increased to 0.3 wt%, the iron crystal structure experiances more corrosion again. It's meaning the nitrogen 0.29 wt% is the best concentration in inhibiting corrosion of iron in liquid lead.

CONCLUSION

Based on the simulation research that has been done in this work, we can make onclusions as following:

1. The best LJ parameters for iron is $\varepsilon = 0.4007(eV)$and$\sigma = 2.3894(\text{Å})$, while for lead$\varepsilon = 0.1910(eV)$and $\sigma = 2.9578(\text{Å})$.
2. The temperature dependence self diffusion coefficient of iron is $D(T) = 1.9069x10^{-7}exp\frac{-135766}{RT}(m^2/s)$, while for lead$D(T) = 1.399x10^{-8}exp\frac{-8885.76}{RT}(m^2/s)$
3. The best corrosion inhibition of iron in liquid lead can be achived when injected by nitrogen at concentration $0.29wt\%$.

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