Effect of temperature on the corrosion inhibition of iron in liquid lead using oxygen inhibitor: studied by MD simulation

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Effect of temperature on the corrosion inhibition of iron in liquid lead using oxygen inhibitor: studied by MD simulation

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Abstract. For corrosion mitigation of steels used in a fast nuclear reactor power plant, oxygen gas is one of promising candidates of inhibitors. Many experiments have been conducted to reveal the mechanism of corrosion and mechanism of how to overcome the corrosion. In the previous work, we had shown computationally that the oxygen atom can be used to reduce the corrosion and we had predicted the oxygen contents. In the current work, not only to explore deeeper the ability of oxygen gas to reduce the corrosion, but also to include the variation of used temperature. We still used iron material to represent a real steels. Using MD (molecular dynamics) simulation based on the Lennard-Jones interaction potential, we sought to understand the concentration of oxygen gas as variation of temperature used in the reactor for the best corrosion mitigation. From this work, we conclude that the temperature does not give effect in related with how concentration of injected oxygen. The temparature merely affects to rise the diffusion coefficient of iron in liquid lead, yet it does not influence how much oxygen needed for corrosion mitigation. In this work, all simulations on different series of temperatures (1023^0K, 1073^0K, 1123^0K, 1173^0K) reveals that oxygen content of 0.1151wt% will cause the lowest corrosion level of iron in liquid lead.

1. Introduction

Molecular dynamics (MD) simulation is a powerful method in computational material sciences. Using MD simulation on many properties of materials under investgation may be predicted or calculated based on specific condition of temperature, pressure, concentration, and others. The purpose of this current study is to determine the corrosion phenomena and its material mitigation, especially the materials used in application of fast nuclear reactors (FNR) design. In FNR that uses liquid metals as a coolant material, for instance lead liquid, the coolant material may cause high corrosion level for steels besides of its important benefits. Many experiments showed the existing high corrosion on the surface of steel materials when they were immersed into high temperature liquid lead coolant [1]. Hence, the focus of the recent researches is to find the proper steels materials or a proper mitigation method to overcome the corrosion phenomena. One of the powerful methods to support the researches is MD simulation. In our previous works, we had shown that iron (representing steels) corrosion can be reduced or minimalized using injection of oxygen/nitrogen for specific and proper concentration [2-7]. We applied MD simulation to predict how much the proper oxygen concentration that would minimize

the corrosion at the lowest level. However, we attempted to examine it merely at 750 C in this research. The focus of the current research is to study the effect of temperature variation during oxygen injection for different concentrations (in %wt). It is designated to find the relation between temperature and required oxygen concentration resulting on the lowest corrosion level of iron. We are still studying the iron to simplify the problem.

1.1 Potential function

One of the important input of MD simulation is potential interaction supporting the interactions among atoms within the material. In this study, we found Fe-O-Pb system that is iron-oxygen-lead atoms system; where Fe is a solid BCC metal, O is oxygen gas and Pb is liquid lead. To simplify the study, we apply Lennard-Jones potential to support the whole atomic interaction inside material system. For liquid or gaseous state, the interaction of atoms is usually represented by Lennard-Jones potential which in general the form is as below,

$$u(r) = k\varepsilon\left[(\sigma/r)^n - (\sigma/r)^m\right] \tag{1}$$

where both σ and ε are the potential parameters and k is a proportional constant in the form of:

$$k = \frac{n}{n-m}\left(\frac{n}{m}\right)^{m/(n-m)} \tag{2}$$

For n = 12 and m = 6, then we have a popular (12-6) Lennard-Jones potential function,

$$u(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right] \tag{3}$$

Following the popular **Lorentz-Berthelot** mixing formula, the interaction among different atoms can be parameterized by:

$$\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2 \tag{4}$$

$$\varepsilon_{AB} = \sqrt{(\varepsilon_{AA} \times \varepsilon_{BB})} \tag{5}$$

Table 1. The Value of Potential Interaction

Pair Interaction	**ε (eV)**	**σ (Å)**
Fe-Fe	0.4007	2.3193
Pb-Pb	0.1910	3.1888
Fe-Pb	0.2766	2.7541
Fe-Pb	0.0639	2.8737
Pb-O	0.0441	3.3084

1.2 Molecular dynamics program

Basically, the MD simulation will solve the Newton 2nd Law of motion, $\boldsymbol{F} = d\boldsymbol{p}/dt$ for specific potential function $u(r)$ numerically. The relation between F and $u(r)$ could be facilitated by $F = -du/dr$. Many MD simulation programs have been developed either simple MD or powerful MD that could be used to compute many properties of materials. In this work, we use Moldy molecular dynamics program created by Keith Refson[8].

2. Simulations and calculations

To understand the effect of oxygen for corrosion inhibition, we calculated the diffusion coefficient $D(T)$ of iron in liquid lead environment, using formulas:

$$MSD = \left\langle \left| \vec{R}(t) - \vec{R}(0) \right|^2 \right\rangle \quad \text{(Mean square displacement)} \quad (6)$$

$$D = \lim_{t\to\infty} MSD/6t \quad \text{(Einstein relation)} \quad (7)$$

Simulations ran for specific ensamble (NPT or NVT or NVE), temperature, pressure, number of atoms, simulation box, molecular structure of material, density of material, number of integration step and time step. In every simulation, we applied the different temperature on different concentrations of oxygen gas. Then, we calculated the diffusion coeficient of iron. We looked for the condition of the lowest diffusion coefficient of iron for certain oxygen concentration which was injected into liquid lead. In our work, we used NPT simulations.

Another important things of MD simulation is equilibration condition. All calculations should be done after simulation achieved equilibration condition. We determined this condition by plotting the energy of system vs integration step (see Fig.1).

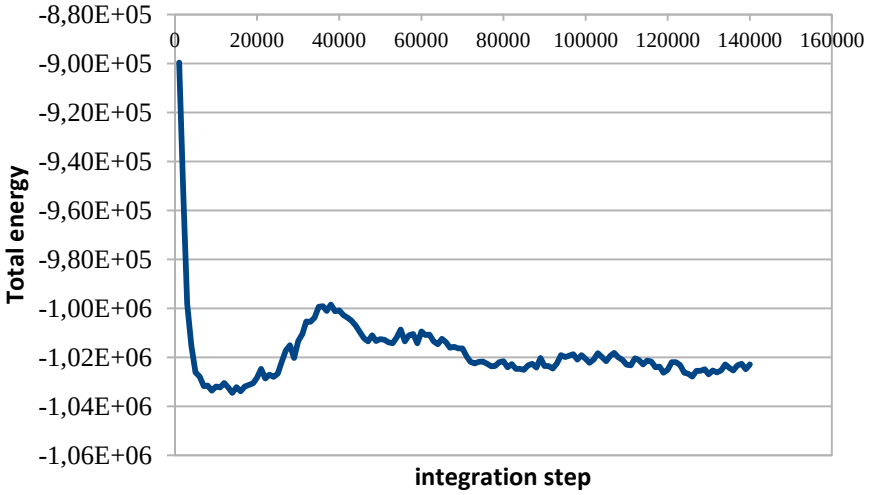

Figure 1. Equilibrium curve of total energy

With Moldy, we can find the information of equilibration condition by typing from terminal with the command =>$moldyext –f 4 name_of_Moldy's_output . From Fig. 1, we computed the properties after 40000 step of integration for better result.

2.1. The material system for moldy input

To realize the simulations, we prepared the material system (Fe-O-Pb) as in Fig. 2 where all the coordinates of material atoms was stored in specific file. The detail number of atoms for every simulation was illustrated in Table 2. Hence, we simulated the material system for every temperature (1023^0K, 1073^0K, 1123^0K, 1173^0K), for every wt% of oxygen (0.0, 0.038, 0.058, 0.0771, 0.1155, 0.1552, 0.1938 nad 0.231). Each simulation ran for pressure 0 atm, for 100000 integration step, for 0.0001 ps of time mesh and for begin-average 40000. We also used the Nosé–Hoover thermostat for constant-temperature molecular dynamics simulations, Andersen constant pressure molecular dynamics simulation, and Beeman algorithm.

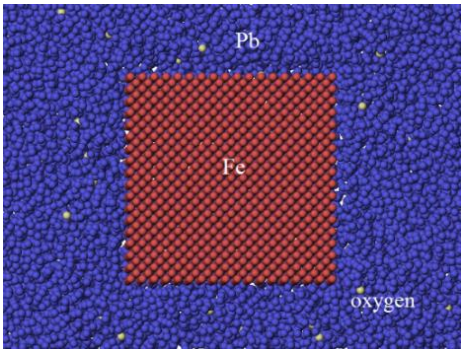

Figure 2. Preparation of material system before simulation

The number of atoms for material system of simulation are as follows:

Table 2. The Simulation Composition of Atoms in Material System before Simulations.

Iron (bcc)	10745	10745	10745	10745	10745	10745	10745	10745
Lead (liquid)	45006	45006	45006	45006	45006	45006	45006	45006
oxygen	0	226	340	450	674	906	1132	1348
Oxygen (in #%)	0.0	0.5	0.75	1.0	1.5	2.0	2.5	3.0
oxygen (in wt%)	0.0	0.038	0.058	0.0771	0.1155	0.1552	0.1938	0.231

3. Results and discussions

Simulations were done using Moldy MD program developed by Keith Refson [8]. This program could be downloaded from website shttp://ccl.net/cca/software/SOURCES/C/moldy/.

Figure 3 illustrates the graphs of iron diffusion D in liquid lead with oxygen injection for different temperatures T calculated by Equation 6 and 7. MSD values can be computed by using Moldy utilities as in manual [8].

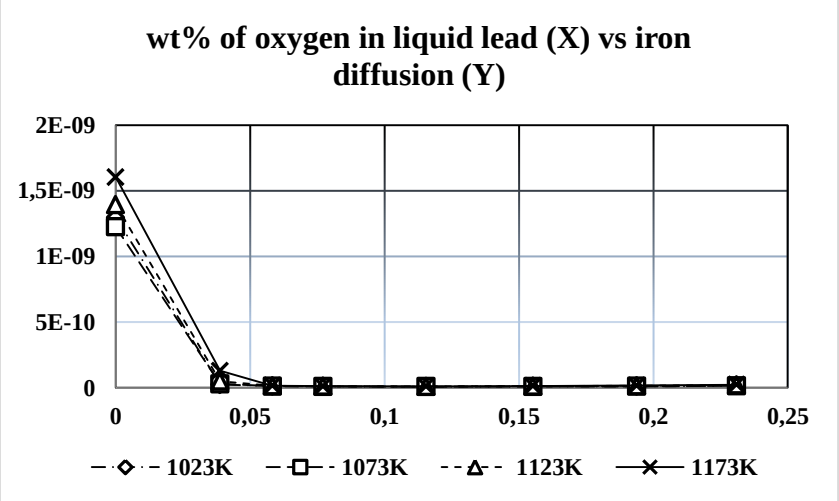

Figure 3(a). Graph of wt% of oxygen vs iron diffusion $D(T)$ in m^2/s.

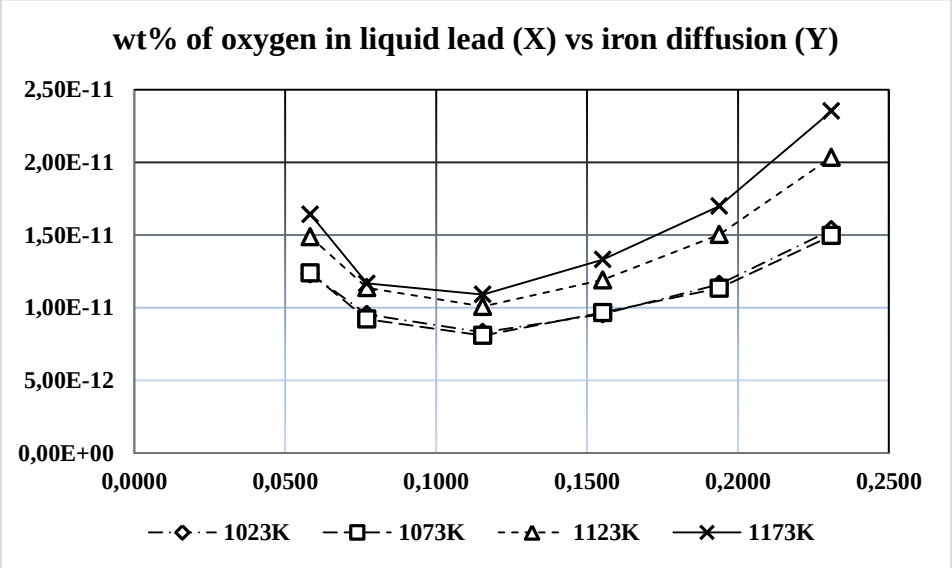

Figure 3(b). Zoom of graph 3(a) for wt% of oxygen more than 0.05wt%

By MD simulation, we can compute the diffusion coefficient of iron in liquid lead as in Fig. 3 (a) and (b) above. Experimental data [1] shows the iron diffusion in liquid lead is about ~ 2.8×10^{-9} m/s^2 for temperature 1023K. The use of 0.1155wt% of oxygen injected into liquid lead reduces the diffusion coefficient significantly from ~ 10^{-9} m/s^2 to ~ 10^{-11} m/s^2 and this occurs for all temperatures. This is about temperature does not effect for the best corrosion inhibition using 0.1155wt% of oxygen.

We could see from these figures that for all series of temperatures (1023^0K, 1073^0K, 1123^0K, 1173^0K) portray the similar trend, and the lowest iron diffusion (corrosion) occurs when the injected oxygen use concentration on 0.1155wt%. From these graphs, the condition in any temperature requires the oxygen content of 0.1155wt% to obtain the lowest iron diffusion (the lowest corrosion attack). The structures of iron after simulation without and with oxygen content demonstrating these combination (0wt%, 1023^0K), (0.038wt%, 1023K) and (0.1155wt%, 1023^0K) could be seen from Fig.4 as below:

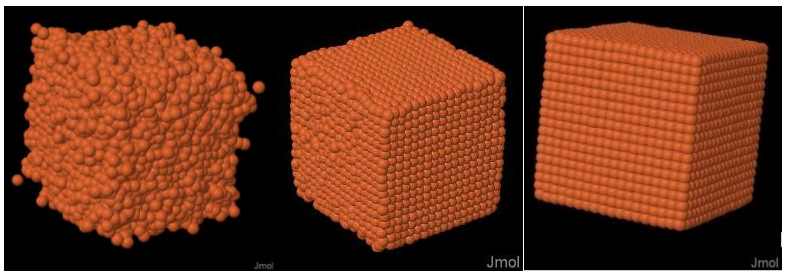

Figure 4. Effect of Oxygen on Iron BCC Structure Stability for Simulation at 1023K (by Jmol) [9]

From the Fig.4 (left), the iron BCC structure after simulation 100000 step without oxygen content shows heavy corrosion. The injection of 0.1151wt% of oxygen (right) shows the best reduction of iron corrosion, whereas the injection of 0.038wt% (middle) still shows relatively high corrosion. Quantitative representation about the effect of oxygen on temperature 1023K, reffering to Fig.4 can be summarized as Table 3.

Table 3. Quantitative Representation about Effect of Oxygen for Temperature 1023^0K

Oxygen content in liquid lead		# Fe before simulation		Fe in BCC after simulation	
# of atom	in %	# of atom	in %	# of atom	in %
0	0%	10745	100%	2739	25.5%
226	0.50%	10745	100%	6739	62.7%
674	1.50%	10745	100%	7471	69.5%

The number of atoms of iron after simulation by oxygen injection (Table 3) can be determined by Ovito code using facility of CNA common neighbour analysis [9].

4. Conclusions and remarks

By applying molecular dynamics simulation, this study proves that corrosion of iron in liquid lead can be reduced maximally using oxygen injection with content of 0.1151wt%. This oxygen content is independent from adjusted temperatures when the corrosion occurs. These simulations were conducted using Lennard-Jones potentials that may be not accurate for metal systems as iron in liquid lead. However for early prediction, we show that the oxygen contents for corrosion mitigation of iron in liquid lead are not affected by adjusted temperatures. In the other words, temperature has no effect towards the influence of the oxygen contents on corrosion mitigation. Eventually, this conclusion needs further and deeper studies for complete explanation of liquid corrosion inhibition and phenomena.

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