

1. Introduction

High-level radioactive waste (HLW) is immobilized in borosilicate glass and sealed in stainless steel canisters for geological disposal. During vitrification, high molybdenum solubility is essential to increase waste loading and prevent formation of a water-soluble yellow phase. Although MoO₃ solubility increases with decreasing glass polymerization^[1], such glasses often show poor chemical durability (Fig. 1).

To achieve both high MoO₃ solubility and good durability, we investigated the SiO₂-B₂O₃-Al₂O₃-ZnO-CaO-Na₂O-Li₂O-MoO₃ system by phase equilibrium experiments and CALPHAD calculations and constructed a thermodynamic database to predict MoO₃ solubility^[2]. However, modeling glass-water reactions remains challenging because dissolution behavior depends on factors such as composition, reaction time, temperature, pH, and sample geometry^[3] (Fig. 2).

In this study, we used a neural network to analyze the relationship between the normalized leaching rate (NLR) of silicon (Si) and glass composition based on Pressure Cooker Test (PCT) data for simulated Japanese HLW glasses. We further combined the neural network model with the thermodynamic model to explore glass compositions that exhibit both high MoO₃ solubility and good chemical durability.

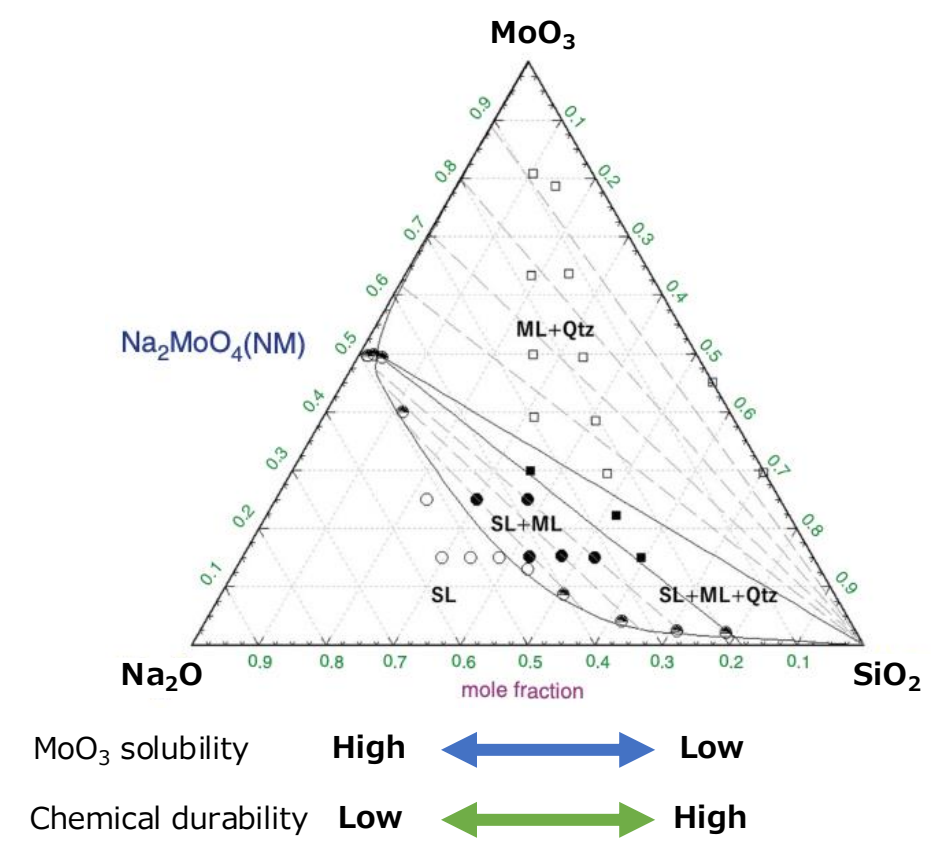


Figure 1. Phase relationship in the system SiO₂-Na₂O-MoO₃ at 1200°C showing phase separation between silicate liquid and molybdate liquid^[1].

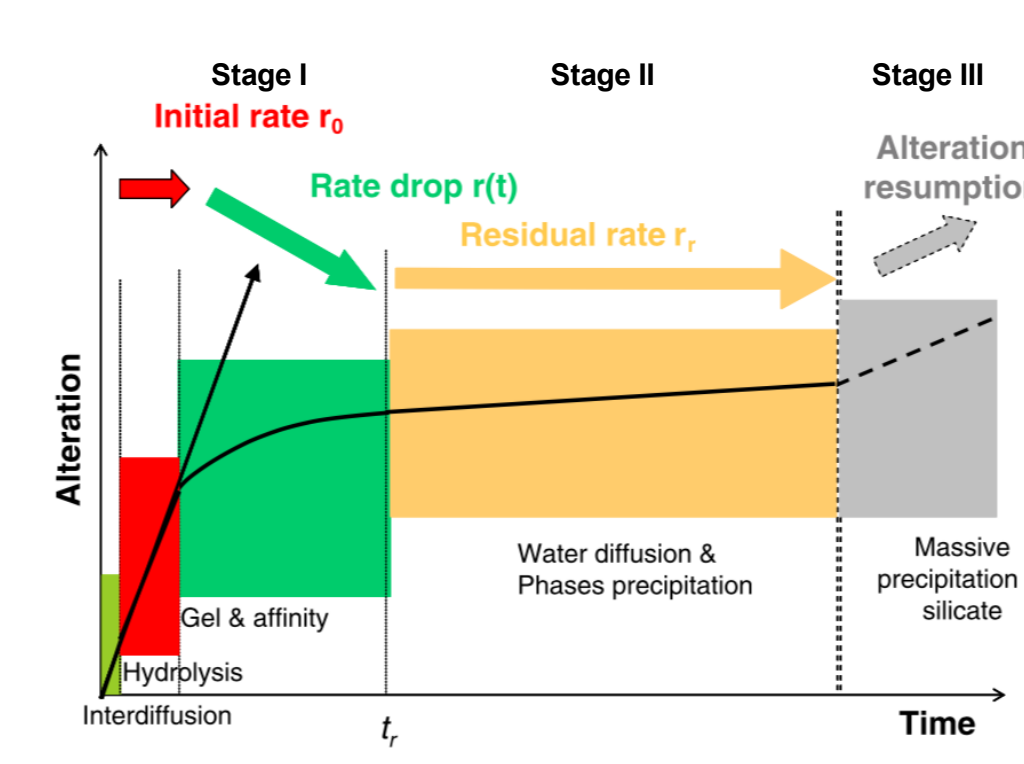


Figure 2. The three successive regimes of the dissolution rate in water of a nuclear borosilicate glass in static conditions: the initial rate, the transition regime, and the residual rate regime^[3].

2. Method

2-1. Dataset

Pressure Cooker Test (PCT) of HLW glass by JNFL
T = 90°C, pH=5.7, Duration=72hours, Pure water,
Normalized leaching rate (NLR) of Si determined by ICP-AES

Table 1. Ranges of glass composition and leaching rate of PCT data.

mol%	SiO ₂	B ₂ O ₃	Al ₂ O ₃	ZnO	CaO	Na ₂ O	Li ₂ O	others	Leaching rate of Si (x10 ⁵)
Max	62.0	27.1	9.0	5.9	7.7	14.6	15.3	12.5	6.50
Min	37.0	10.4	1.3	0.0	0.0	3.3	0.0	3.4	0.38

Number of data (N=178)
Original data : 128
Oversampling data : 50
Test data : 10
The data was split into training and validation in the ratio of 80% and 20%.

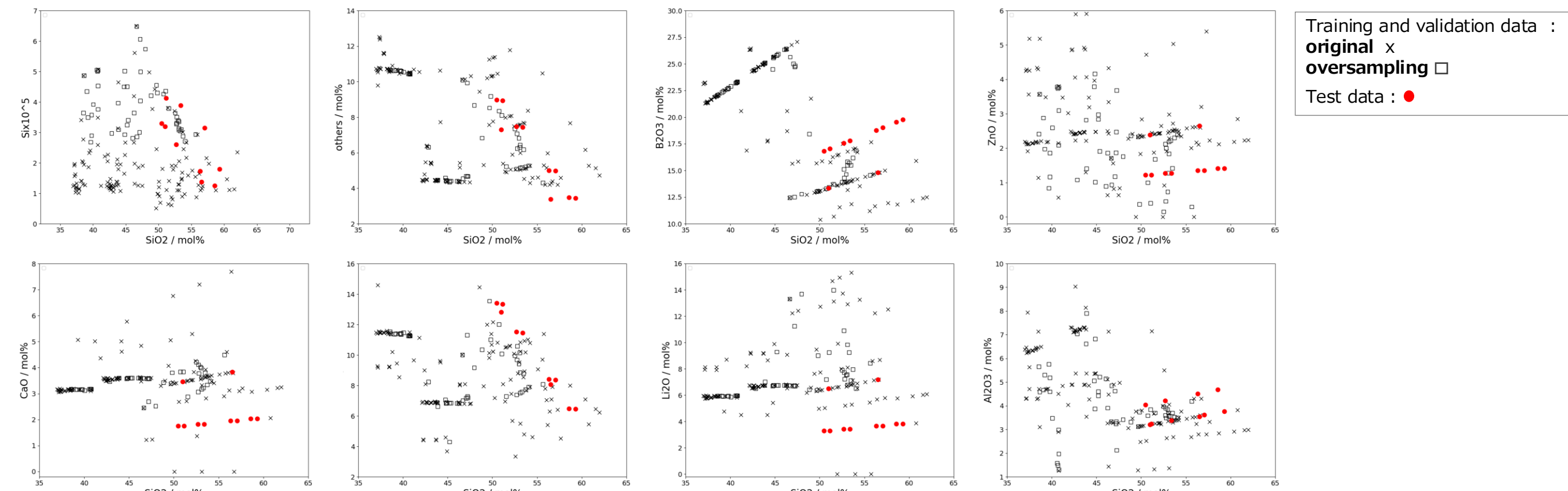


Figure 3. NLR of Si and chemical composition of glasses of PCT data. Data oversampling was performed by SMOTE^[4] to mitigate data imbalance. The oversampling increases the number of samples in the sparse regions.

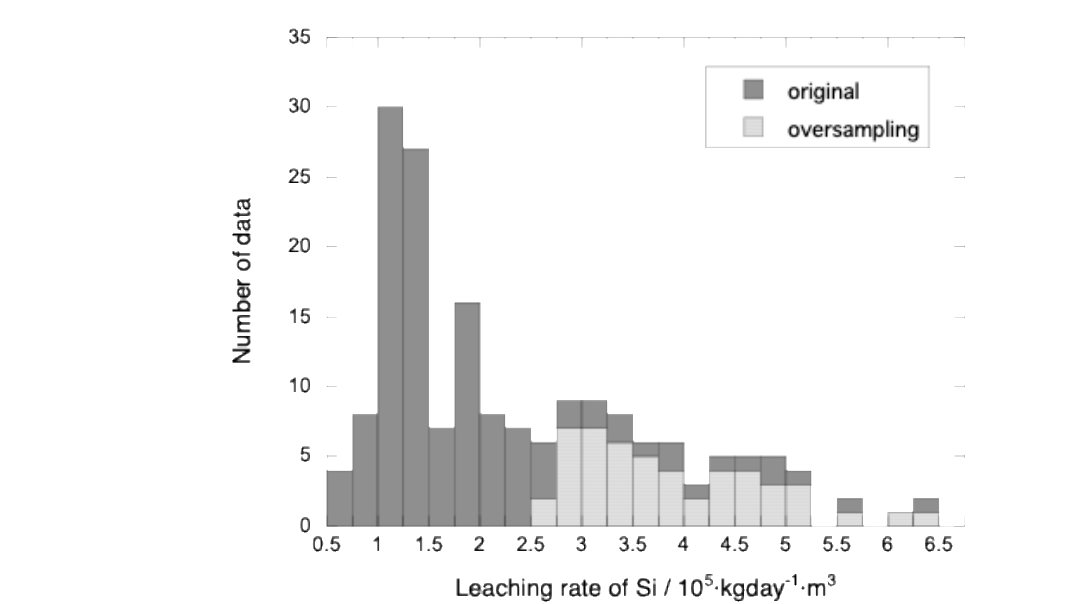


Figure 4. Comparison of the distribution of NLR before and after oversampling.

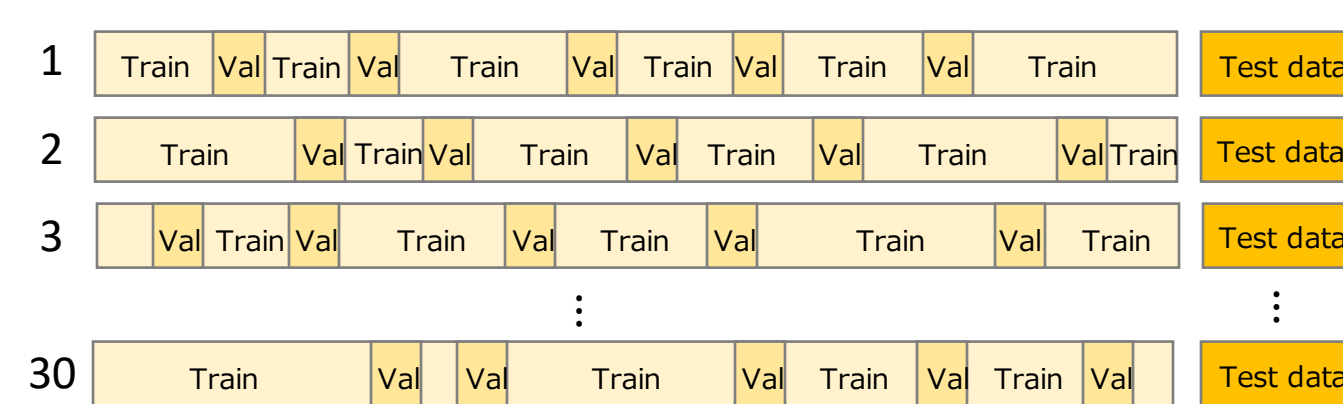


Figure 5. Schematic illustration of different data-splitting strategies for model training (Train), validation (Val), and testing (Test data). Different configurations correspond to various cross-validation or hold-out approaches.

3. Results

Comparisons of Root mean square error (RMSE)

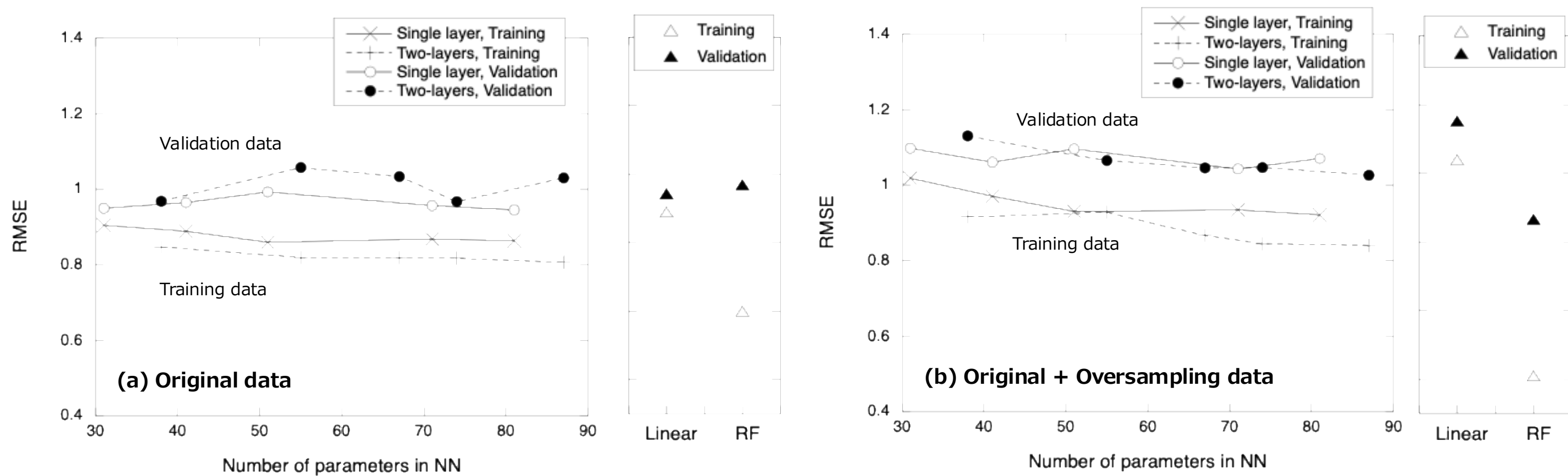


Figure 7. RMSE of neural network (NN), linear regression, and random forest (RF) models on the test dataset. (a) Original data, (b) Original + Oversampling data, (c) Test data.

- The RMSE of NN showed little dependence on network size for the original, oversampled, and test datasets.
- Random forest models tended to overfit.
- Models trained with oversampled data (SMOTE) show lower RMSE of Test data compared to those trained on the original dataset.
- Neural networks achieved lower RMSE than linear regression for all datasets.
- For the same number of parameters in the NN, two-layer models were more accurate than one-layer models.

Search for glass compositions combining high MoO₃ solubility and chemical durability

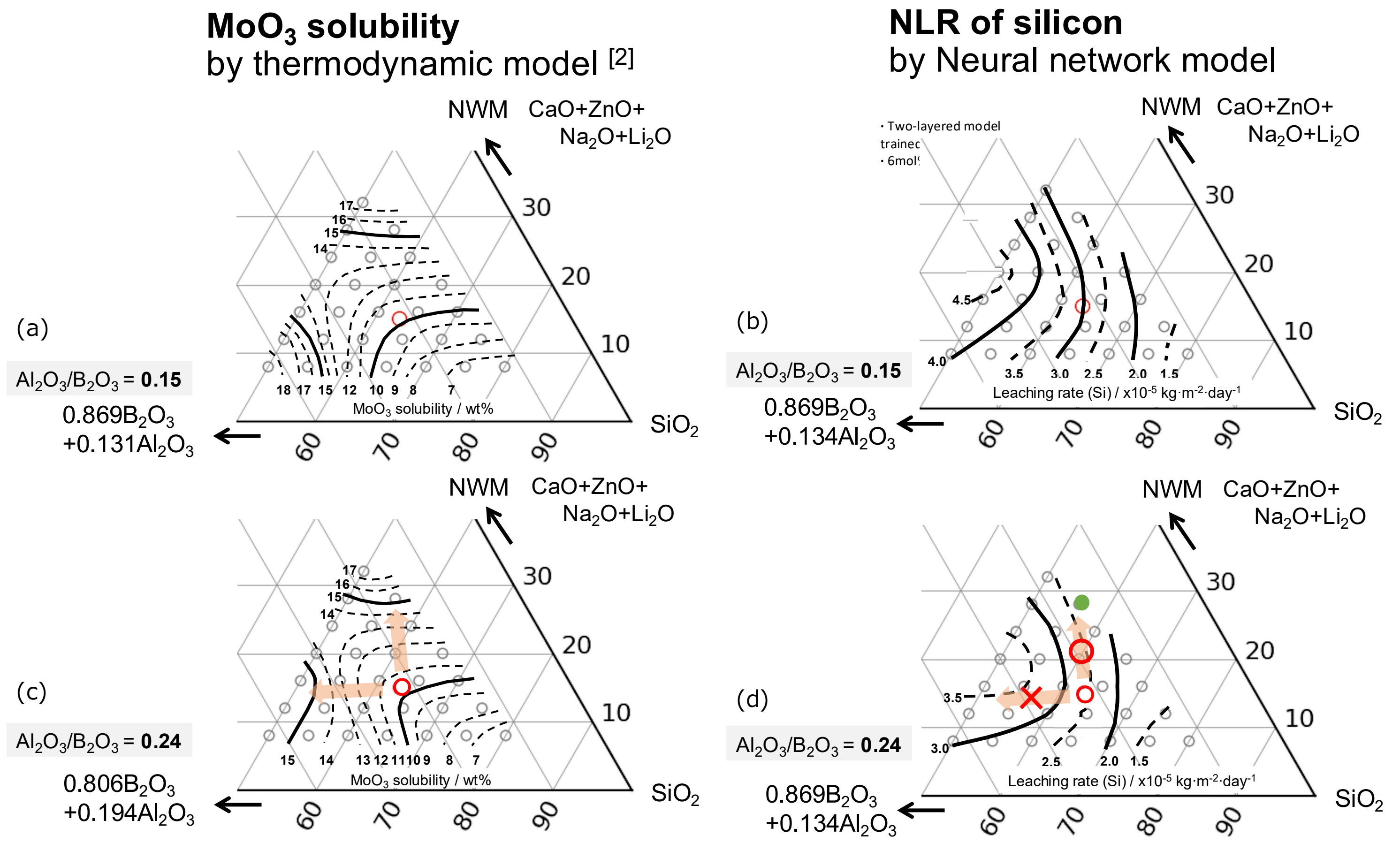


Figure 8. Comparison between calculated and measured NLR of Si (10⁵·kg·day⁻³·m³) for test data. Error bars show standard deviation of 30 times calculations (Fig. 5).

Figure 9. Ternary contours of (a, c) MoO₃ solubility at 1200°C by thermodynamic model and (b, d) NLR of Si by neural network model in the pseudo ternary system (CaO+ZnO+Na₂O+Li₂O)-(B₂O₃+Al₂O₃)-SiO₂.

Table 2. Comparison of the current and improved glass compositions, and the predicted MoO₃ solubility and the predicted NLR of Si.

mol%	Current glass composition (○)	Improved glass composition (●)
SiO ₂	53.2	49.8
B ₂ O ₃	13.9	11.5
Al ₂ O ₃	3.3	2.8
ZnO	2.5	3.8
CaO	3.6	5.5
Na ₂ O	10.6	10.3
Li ₂ O	6.8	10.3
Others	6.0	6.0
Predicted values		
MoO ₃ solubility / wt%	11.1±2.8	15.2±2.8
Si Leaching rate / x10 ⁻⁵ ·kg·m ⁻² ·day ⁻¹	3.0±0.9	2.6±1.3

< Method > The glass composition was normalized into three components: SiO₂, monovalent + divalent oxides (CaO + ZnO + Na₂O + Li₂O, NWM), and (B₂O₃ + Al₂O₃). Calculations were performed around the current glass composition at 1200°C, with a fixed waste content of 6 mol% and Al₂O₃/B₂O₃ ratios of 0.15 or 0.24. The NLR was predicted using the two-layer neural network model (Node=4-3) developed in this study, and MoO₃ solubility was obtained from a thermodynamic calculation^[2]. Both results are presented as pseudo-ternary contour maps (Fig. 9).

Two compositional trends were identified for increasing MoO₃ solubility relative to the current glass:
The calculations revealed two compositional modifications that can enhance MoO₃ solubility compared with the current glass:

- (Case-1) Decreasing SiO₂/(Al₂O₃ + B₂O₃) while keeping NWM constant.
- (Case-2) Increasing NWM while keeping the SiO₂/(Al₂O₃ + B₂O₃) ratio constant.

Evaluation of the NLR indicated that the Case-2 can increase MoO₃ solubility while reducing NLR. The corresponding glass compositions are listed in Table 2.