Title: Assessing static glass leaching predictions from large datasets using machine learning.

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Keywords

Glass Leaching; Machine Learning; ALTGLASS; Dissolution Prediction

Abstract

Radioactive waste vitrified within glass is planned to be ultimately disposed of within a geological disposal facility. This study has applied machine learning to predict static glass leaching using an international experimental database of approximately 450 glasses to train/test various algorithms. Machine learning can accurately predict B, Li, Na, and Si releases for this complex database with Tree-based algorithms (notably 'BaggingRegressor' and 'RandomForestRegressor' in Python). This is provided that leaching experiment results, including elemental releases, are incorporated within the algorithm training variables, given that this study finds inaccurate prediction solely using initial test parameters as features. The trained algorithms underwent additional testing using an external database with prediction showing worse performance, likely due to substantial MgO and Na_2O pristine glass oxide compositional variations across databases, with B releases generally being overestimated and Na underestimated. The use of molar oxide content performed significantly better than weight-fraction oxide for learning.

1. Introduction

The UK nuclear industry intends to ultimately dispose of its vitrified radioactive waste glass inventory deep underground within a geological disposal facility (GDF). To achieve this aim, the regulatory safety case will require robust radionuclide migration models which appropriately quantify glass dissolution uncertainty due to the various glass compositions, groundwater compositions, and leaching conditions that may be present within a repository. Machine learning may be a valuable tool for correlating large-scale dissolution data, with a recent study having successfully predicted UK and international waste glass dissolution behaviour from static and dynamic leaching experiments [1]. Such methods have a potential advantage from not making assumptions about glass alteration behaviour like in reactive-transport mechanistic models. However, considering the relatively small compositional ranges and test conditions used in this previous study, there has been a need to examine machine learning dissolution prediction using a significantly larger and more diverse dataset. Here, this study aims to build upon this previous work by firstly applying machine learning to a large international glass dissolution database. Secondly, it aims to examine the transferability of the trained algorithms derived from data measured separately by many organisations to predict other independent data.

2. Methods

Machine learning algorithms (multiple-linear, Lasso, Ridge, Elastic-net, support-vector machine (SVM), gradient boosting, bagged random forest, single-layer feed-forward neural networks, random forest regression) of varying complexity were applied to predict B, Li, Na, and Si elemental concentrations and normalised releases (Section 2.2) from experimental features (including glass composition, glass density, dissolution temperature, solution pH, elemental concentrations/releases). Algorithms were both trained and tested using ALTGLASS data (Section 2.1), and the trained algorithms were subsequently applied to independent experimental data (Section 2.2). Algorithm performance was assessed via R^2/mean square error (MSE) metrics. MSE was computed using

Equation 1 considering each *measured observation i* ($y_{i,m}$), *predicted observation i* ($y_{i,p}$), and *n observations.*

$$\text{MSE} = \frac{\sum_{i=1}^{n} (y_{i,m} - y_{i,p})^2}{n} \qquad \textit{Equation 1}$$

Training data was obtained only using the ALTGLASS database by partitioning the available experimental leaching data using random sampling, splitting training and test data with a five-fold cross validation (three repeats) method. Five-fold cross-validation was also applied on the training data to optimise various model hyper-parameters in Python. The full set of variables extracted from the ALTGLASS (and similarly independent database) were: leaching test duration, glass surface area to leachant volume (SA/V), glass density, nominal glass mass, nominal leachant volume, composition (see Table S1 for oxide members), pH (in time), and Si, Li, Na, and B concentrations in solution in time. These were used as they represent the most important variables in leaching experiments and allowed minimal loss of experimental information across the two databases.

Simulations were performed to predict Si, Li, Na, or B concentrations (μg/ml) and for these, composition was considered either on a mol. % or wt. % oxide basis. Alternatively, Si, Li, Na, or B releases (g m^{-2}) (Section 2.2) were predicted having treated composition on a mass fraction by element basis. For any given simulation, Si, Li, Na, or B concentrations/releases were predicted using the remaining variables as learning features. For example, when predicting B release at each time (Figures 1-3), the leaching time, SA/V, glass density, nominal glass mass, nominal leachant volume, composition, pH (in time), and Si, Li, Na release were all used as input variables. As another example when predicting Si release, all variables excluding Si release were used for algorithm training. Note that other simulations were additionally performed to examine the ability of machine learning to predict each species concentration/release solely from experimental setup conditions (leaching test duration, SA/V, glass density, nominal glass mass, nominal leachant volume, and composition only). The two databases are now described; See Table S1 for mean and standard deviation mol. % oxide dataset values.

2.1. ALTGLASS Database

The ALTGLASS database [2] version 3.0 contains ~2600 observations of static glass dissolution data from approximately 450 glasses, obtained following ASTM product consistency test (PCT) A and B methods [3]. High-level and low activity waste (HLW and LAW, respectively) glass compositions are included (both radioactive and simulant), provided by the international nuclear community, curated by Savannah National River Laboratory (SRNL). A broad range of test durations (from a few hours to timescales exceeding 7426 days), SA/V (1.1-39.1 m^2/L), temperatures (25-200 °C), leachate pHs (7.39-13.66), glass compositions (wt. % oxide), and leachate elemental concentrations (µg/ml) are recorded. Leaching data covers a broad range of alteration regimes, although the ALTGLASS database only includes a limited number of experiments of high enough leaching duration for stage V dissolution (resumption of the initial alteration rate) [2].

2.2. Independent Experimental Data

To independently test the ALTGLASS trained algorithms, a separate large database has been established (~970 observations), using various UK vitrification campaign (National Nuclear Laboratory) Magnox-THORP Blend, Ca/Zn, and post-operational clean-out (POCO) glass 90 °C deionised water leaching data. Additional contributions include: various temperature dissolution experiments performed at the University of Cambridge with Mixture-Windscale 25 wt. % simulant Magnox loading (MW25) [4], lithium-doped International Simple Glass (ISG) [5], simple binary-alkali (Li-Na) borosilicate glasses (submitted for publication); French CJ glasses [6]; and long-term static leaching experiments (MW and SON68) [7]. The database draws together experimental information that was previously recorded independently by different research organisations.

Considering the lack of short-term leaching ALTGLASS results of less than 7 days duration, additional experimental data has been generated in this time range. To this end, ISG and MW25 glasses were crushed and sieved to achieve a particle size of 75-150 µm, ultrasonically cleaned in absolute ethanol following the ASTM methodology [3], dried at 90 °C, and magnetically filtered. Static leaching experiments followed the ASTM PCT-B method [3] using type 1 deionised water (18.2 MΩ.cm at 25.0 °C) as leachant. Experiments used between 0.375 and 0.4 g sample (MW25/ISG powder) leached at 40 and 90 °C in 4 mL of water (targeting a geometrical SA/V of 2000 m^{-1}).

Measurements were taken at 1 hour, 3 hour, 5 hour, 1 day, and 7 day intervals with each being taken from a separate stainless steel vessel with PTFE liner. Triplicate experiments were performed using independent reactors (together with two solution blanks), with pH also being measured. Elemental concentrations of glass species (all ISG species and the major species of MW25) were measured by inductively coupled plasma mass spectrometry (ICP-MS). Normalised species releases (g m^{-2}) were computed by normalising the background and dilution corrected elemental concentrations to the SA/V and mass fraction of that element within the glass (dimensionless). See Figures S1 and S2 for pH and measured release data.

3. Results

3.1. ALTGLASS vs Independent Data Machine Learning Performance

Figure 1 presents predicted against measured B, Li, Na, and Si releases using ALTGLASS and independent data using the highest performing algorithm *'BaggingRegressor'* (Section 3.2). This algorithm [8] works by aggregating the predictions of many regressors each fit on random data subsets, and here, hyperparameter optimisation used a range of 1 to 300 estimators (increments of 10), with optimisation performed on negative mean square error. Perfect performance would have data points lying along the dashed lines in Figure 1. For ALTGLASS test data (not part of training set), predicted releases were strongly correlated with experimentally measured values (B, Li, Na, and Si). Values were not disproportionately under or over-estimated across the four species. Errors increased when testing on independent data (not part of the ALTGLASS database), with release errors typically being overestimated for B, underestimated for Li, becoming more substantial with increasing Na releases, and primarily overestimated for Si with predictions being restricted to less than approximately 1.8 g m^{-2}. Note that several Si releases were substantially underestimated as further described in a subsequent publication, likely due in part to the relatively high SiO_2 content in the specific glasses relative to the overall ALTGLASS database. The content of these four component (Si, B, Na, Li) glasses is provided in Table S2.

FIGURE 1

3.2. Algorithm Performance

Figure 2 compares MSE errors on the release predictions as a function of learning algorithm for both sets of test data. Considering all four species, errors were found to be lowest for the 'BaggingRegressor' and 'RandomForestRegressor' algorithms. Similar behaviour was observed for concentration (μg/ml) prediction, with errors also being lower when considering compositional features on a mol. % oxide rather than wt. % oxide basis in the algorithm learning.

FIGURE 2

3.3. Observed Leaching Profiles

Figure 3 shows predicted/measured B releases for several experiments within the test data (independent of ALTGLASS). Predicted B releases are shown to be overestimated in several cases, as is consistent with Figure 1, despite trends in the leaching behaviour being generally preserved.

FIGURE 3

4. Discussion

Predicting glass dissolution is of vital importance for the nuclear industry and its plans for geological disposal. This study has aimed to understand if machine learning can predict static glass leaching on a substantially larger and more diverse international database than previous work [1]. This database was chosen as the compositions are extremely relevant to the international nuclear industry and it is one of the most extensive databases publicly available. One of the advantages offered by applying machine learning in this study is that no explicit assumptions about glass dissolution mechanisms have been made. Mechanistic models, for example, in reactive-transport modelling, frequently assume glass alteration behaviour, and they remain to be fully validated and parametrised over a wide range of glass compositions and leaching conditions [9–11]. As an example, there is still debate on whether glasses corrode following diffusion-based or interfacial dissolution-reprecipitation models [12–14]. Moreover, uncertainties remain regarding secondary phase composition, passivating capabilities of the altered layers, and passivating reactive interface/depleted gel end-members. Generally, there has

been a need to better explore the use of large-scale data, particularly as leaching experiments take considerable time, and to see if machine learning might be used as an alternative prediction method.

This study has showed that machine learning was able to predict the four major glass species, B, Li, Na, and Si static leaching behaviour reasonably accurately in the ALTGLASS database (Figure 1), depending on the algorithm (Figure 2) and features used. Therefore, machine learning may be used as a benchmark for similar compositions to check for experimental/compositional anomalies. Errors were found to increase when predicting independent data using ALTGLASS trained algorithms. This may have been either due to the substantial difference in composition between the complex glasses of the ALTGLASS database and the more simplistic glasses of the independent data, or differences in leaching experimental design. For example, owing to significant differences between ALTGLASS and the independent data leaching test durations, or general differences between database compositions as the independent data used here (comprising Magnox-THORP Blend, Ca/Zn, and POCO glasses) typically had higher MgO and lower Na_2O oxide compositions than that of ALTGLASS. Nonetheless, machine learning could preserve general leaching behaviour trends, particularly for B, even when the values were often overestimated (Figure 3), and therefore, it might be used as a test of consistency in newly acquired data. The 'BaggingRegressor' and 'RandomForestRegressor' algorithms overall performed best for predicting releases (followed by gradient boosting), with Na release identified as the most important of the training features (Section 2) for accurate B learning. The same algorithms performed best for concentration (µg/ml) prediction, with it being found that mol. % oxide features gave better learning performance than wt. % oxide species; likely due to higher mass species being given greater feature importance in learning when wt. % oxide features were used. Therefore, it is suggested that future machine learning studies consider these ensemble methods as a benchmark, use mol. % oxide composition and not wt. % oxide for compositional learning features, and note the stronger learning importance of Na release on B release prediction over other features (including pH, and Si/Li release).

Machine learning and data analytics in general can be used to support glass corrosion understanding. For example, Figure S3 presents the correlation between different learning features and B release in the ALTGLASS data, highlighting that B release increases with pH, Li release, Li, Mg mass fraction

by element, and with decreasing Al, Ca, Si mass fraction by element, etc. These results are supported by or support current glass alteration understanding. Machine learning might also be used to understand how different glass compositions influence prediction accuracy, potentially identifying compositions for further study. For example, by analysing the correlation between relative predicted-test B release errors and compositional learning features within the independent data, errors were found to have highest positive correlation with Zn, Zr, and Ca mass fraction by element and most negative correlation with Mg. This may be partly due to the strong stabilising effect of Ca, Zn, and Zr (and destabilising effect of Mg) [7,15,16] which causes increasingly significant changes and unpredictability in B release as the contribution of each respective element is relatively modified within the pristine glass.

Importantly, machine learning could accurately predict B, Li, Na, and Si glass static leaching behaviour using the large-scale ALTGLASS international data, provided remaining concentration data, for example, that of Li, Na, Si in the case of B prediction, were used for learning. Significant errors were observed when solely using experimental setup parameters as features, and therefore for prediction only from experimental setup parameters, machine learning may not offer significant advantages in static leaching prediction over mechanistic models. Overall, results suggest that algorithm predictions cannot replace newly generated experimental leaching data, and that either more data is needed for prediction from experimental setup variables, or that machine learning methods may be more valuable for identifying glass compositional outliers which would require additional consideration or assist in the interpretation of new data, assuming the underlying training set utilises appropriate experimental parameter ranges. In future work, it would be interesting to understand whether machine learning can accurately predict static glass dissolution solely from experimental features within simplistic compositional matrices, and how diverse these can be before prediction performance weakens.

5. Conclusions

One of the aims of this study has been to extend previous work [1] and apply machine learning to a substantially larger and more diverse international database. A repeated observation has been that

predictive errors increase significantly when predicting leaching behaviour purely from experimental setup conditions, which naturally includes the pristine glass composition. It therefore remains to be shown that machine learning can predict dissolution results (for example, B release) independently of evolving experimental conditions i.e., without including leachate pH or Na release, for example, as learning features. Consequently, it may be better to use machine learning as a tool for correlating large-scale data to identify compositional outliers on the basis that the training data uses appropriate compositional bounds, or to guide dissolution data interpretation, rather than as a complete replacement tool for experiments.

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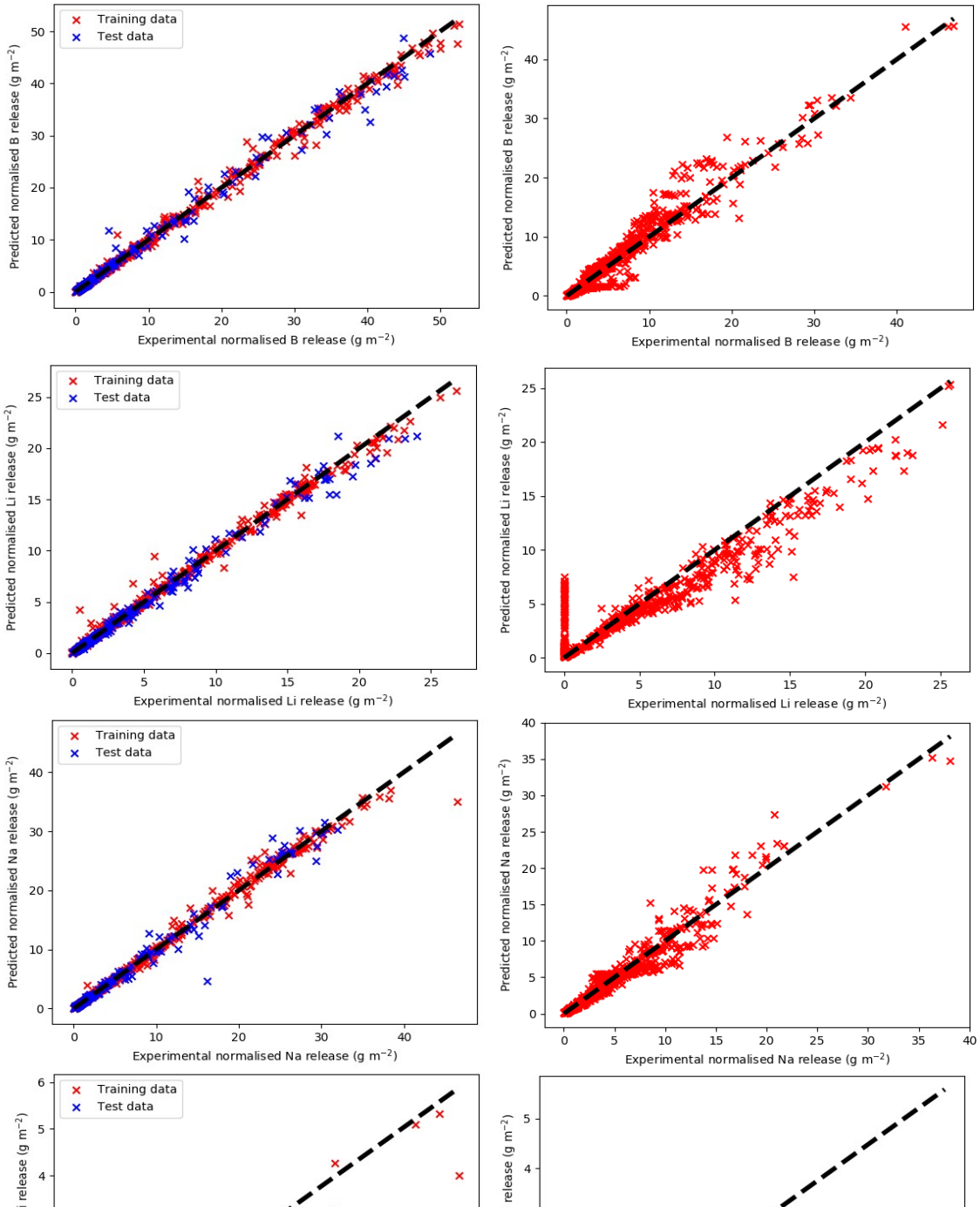
Figure 1


Training data
Test data
Predicted normalised B release (g m^{-2})
Experimental normalised B release (g m^{-2})
Predicted normalised Li release (g m^{-2})
Experimental normalised Li release (g m^{-2})
Predicted normalised Na release (g m^{-2})
Experimental normalised Na release (g m^{-2})

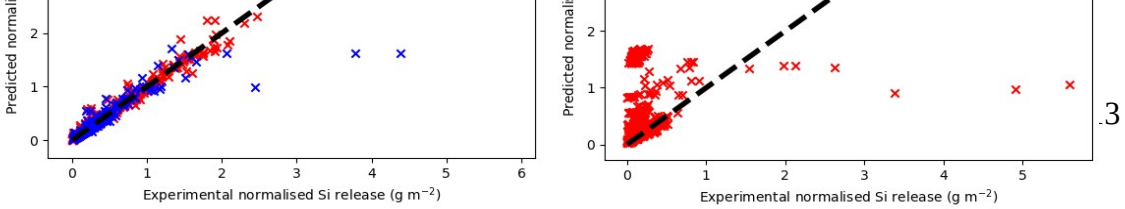


Figure 1: Predicted versus measured normalised releases for B, Li, Na, and Si, for ALTGLASS training/test data [Left figures] and independent data [Right figures]. The 'BaggingRegressor' method was applied, considering experimental setup conditions (temperature, SA/V, composition, etc.), leachate pH, and other species releases input features for learning. Perfect datapoints would follow dashed black lines. Several of the extremely underestimated Si releases are to be discussed in a subsequent publication.

Figure 2

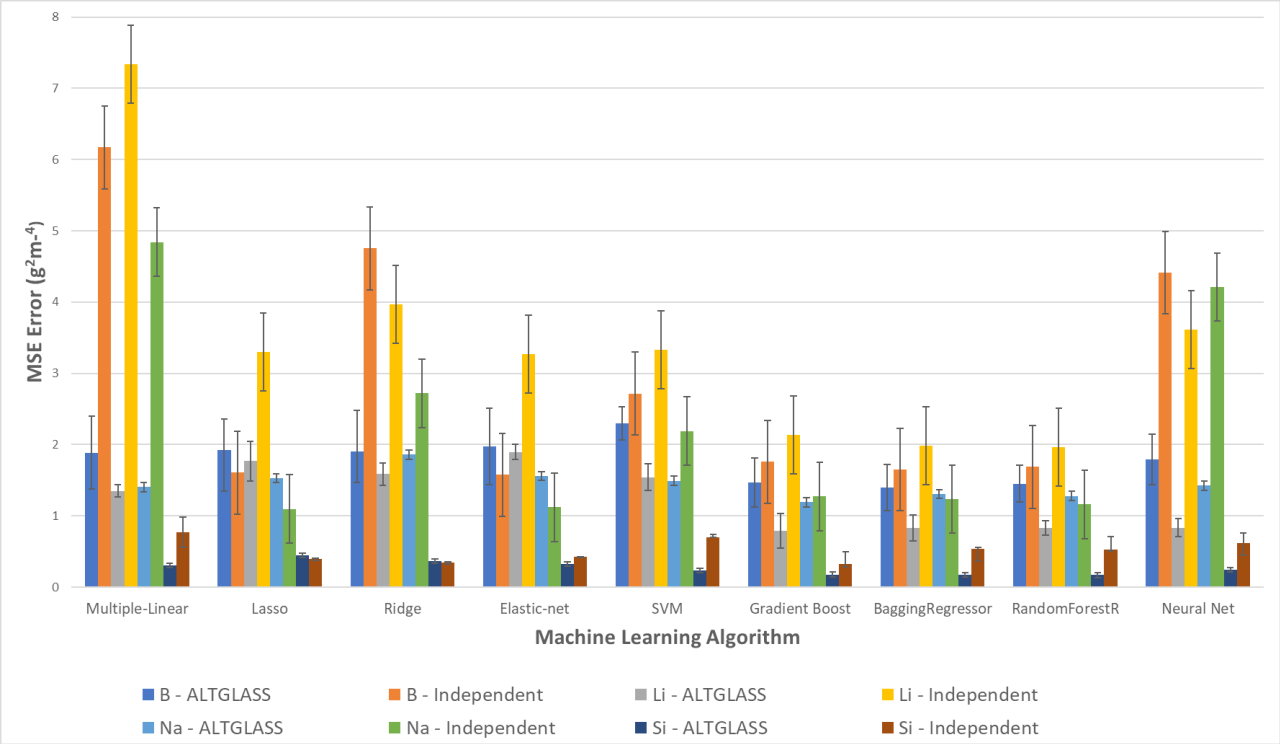


Figure 2: MSE errors on the ALTGLASS test and independent B, Li, Na, and Si test release data as a function of machine learning algorithm. All available features were used for algorithm learning.

Figure 3

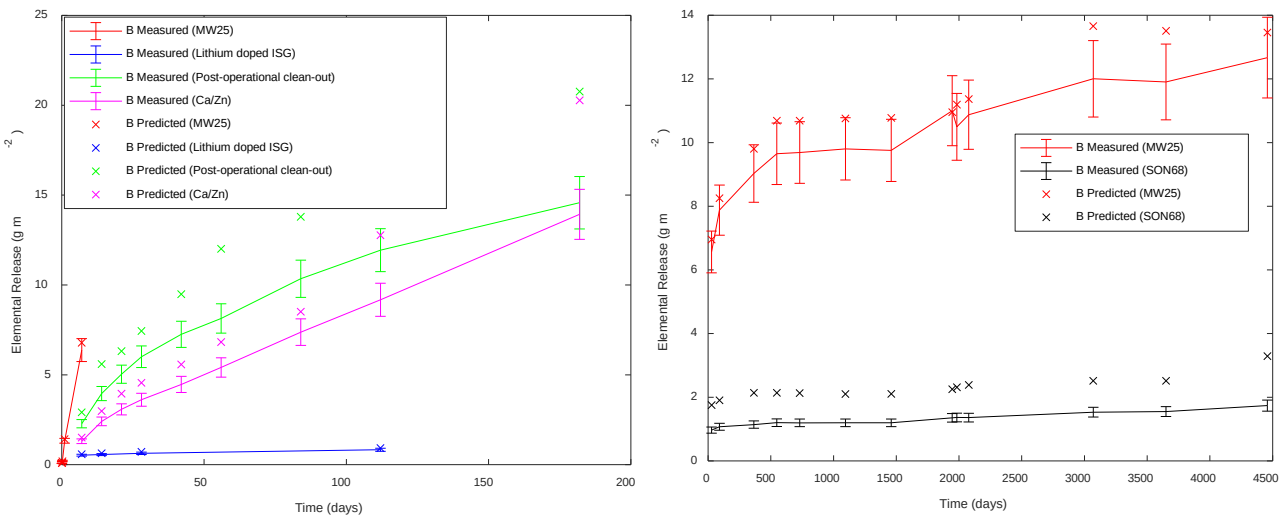


Figure 3: Example predicted/measured B release curves for the independent data ('BaggingRegressor'). The full features (experimental setup parameters, leachate pH, Na/Si/Li releases, etc.) were used for algorithm learning.

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