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Peer-review status

This manuscript is a non-peer-reviewed preprint submitted to EarthArXiv. It has not yet been submitted to a journal. Later versions of this preprint will note the journal submission and, if accepted, the published DOI.

Preprint version 3, October 2026.

Code and data: the LixaLearn v0.3.0 source code, the synthetic benchmark, the scripts behind every number and figure, and the worked example are available from the author on request by email (shahram.asgari@uga.edu).

Data-efficient prediction of rare earth leaching from industrial residues with physics-constrained machine learning

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Abstract.

Coal ash, mine-water sludge, red mud and phosphogypsum contain rare earth elements, and each new feedstock needs its own leaching recipe. LixaLearn couples a small neural network to closed-form rate laws for four metal hosts (exchange sites, fast-dissolving minerals, slow-dissolving minerals and a locked fraction), with part of the fast host limited by the solubility of its mineral. The network maps bulk chemistry to 17 rate-law parameters, and one to three laboratory test runs on a new feedstock update them. On 175 synthetic feedstocks of seven types, the error on unseen recipes after three test runs was 5.4 percentage points, against 6.7 for tuned gradient boosting and 5.7 for a network without rate laws. The method was then developed on real data in the open. An earlier version failed a pre-registered test on 57 phosphogypsum runs, because its rate laws had no solubility limit; with a solubility-limited host and the common-ion effect of sulfate, three test runs predicted the other runs to 7.4 points, against 10.9 for gradient boosting and 11.5 for the network without rate laws (a development result). In the final held-out test, on 29 runs of an ion-adsorption clay, LixaLearn beat gradient boosting (3.3 against 5.5 points) and the direct network (12.3), but not the mean of the three test runs (2.7), and it did not rank the clay runs. On red mud leached with citric acid, the machine-learning models remained better. Physics-constrained learning transferred to real feedstocks where its rate laws had the right structure, and checking that structure on a few complete runs should come before using it on a new kind of feedstock.

Keywords: rare earth elements; critical minerals; leaching; hybrid modelling; physics-constrained machine learning; few-shot learning; phosphogypsum; ion-adsorption clay; red mud; pre-registered test

1 Introduction

Rare earth elements go into permanent magnets for motors and wind turbines, and their supply is concentrated in a few countries (U.S. Geological Survey, 2025). Industrial residues offer a second supply that has already been mined and ground. Rare earths occur in coal fly ash (Taggart et al., 2016), in the solids from treating coal mine drainage (McDevitt et al., 2024), in phosphogypsum from fertiliser production (Li et al., 2022) and in red mud from alumina refining (Borra et al., 2015). Pilot plants that recover critical minerals from such by-products are now being funded (U.S. Department of Energy, 2025). What these residues have in common is variety: their chemistry changes from one source to the next, and often from one batch to the next.

That variety is the problem this paper addresses. How a residue releases its rare earths depends on where the metal sits in the solid. Rare earths held on clay surfaces are swapped off by a salt solution (Moldoveanu and Papangelakis, 2012), those inside glassy ash particles need strong acid and heat, and calcite and other carbonates consume acid before it reaches the metal. Here a recipe means the reagent and its dose, the temperature, the grain size, the liquid-to-solid ratio and the contact time. A recipe that

works for one residue can therefore fail for another of the same kind, and each new sample needs its own series of bench tests before a leaching design, such as one made with Lixa (Asgari, 2026), can start. A model that predicts a new residue from a handful of tests would shorten that series.

Machine learning has been used to shorten this search. Nguyen et al. (2025) trained gradient-boosted trees on 572 leaching experiments from the literature and reached a coefficient of determination of 0.81 on held-out experiments. On an independent external dataset the mean absolute error rose to 19.4, which the authors attribute to domain shift. A model that maps inputs straight to recovery has no notion of where the metal is, so it cannot carry what it learned about one feedstock to another. Hybrid models address this by letting a neural network supply the parameters of a mechanistic model (Psichogios and Ungar, 1992). The mechanistic part limits the answers to physically possible ones and needs fewer data (Karniadakis et al., 2021; Willard et al., 2022).

This paper applies that idea to leaching and asks three questions. First, with the same data, does a model with leaching rate laws predict a new feedstock better than models without them? Second, how many test runs on the new feedstock are needed? Third, are the predictions good enough to rank recipes? The model, LixaLearn, couples a small neural network to closed-form rate laws for four metal hosts (Fig. 1). The network guesses the host shares and rates from the bulk chemistry, and one to three test runs on the new feedstock correct the guess. The recipe enters only through the rate laws, so a feedstock described once can be predicted for any recipe. The ranked recipes can then be passed to Lixa, an image-informed leaching design framework (Asgari, 2026), for scale-up.

Leaching curves with a known answer are scarce. Most published kinetics exist only as figures, and no published dataset states where the metal sits. The main test therefore uses synthetic feedstocks generated with Lixa's batch model. Three real datasets then check the method on measured data: red mud (Ray et al., 2025) and phosphogypsum (Li et al., 2022), which shaped the model, and an ion-adsorption clay (Anawati, 2022), kept apart and used once as the final test. Each failure along the way is reported, together with the change it led to. Section 2 describes the model and the tests, Sect. 3 the results and Sect. 4 their meaning and limits. Appendix A follows one feedstock through the method, and Appendix B lists the settings of the synthetic data.

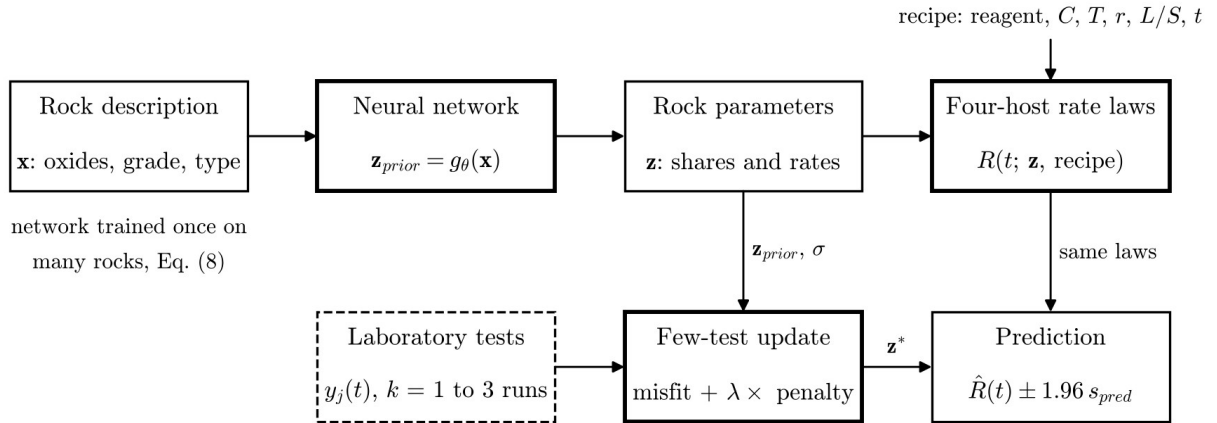


Figure 1. Structure of LixaLearn. A neural network maps the feedstock description to the parameters of the four-host rate laws, which give recovery for any recipe. For a new feedstock, one to three laboratory test runs update the network's guess before prediction. Thick boxes are the three parts of the method; the dashed box is the only new data a new feedstock needs.

2 Methods

2.1 Four metal hosts

A feedstock holds its metal in up to four hosts (Fig. 2). On **exchange sites**, the metal is held by charge on clay or oxide surfaces, and another cation in the solution swaps it off without dissolving any mineral. In **fast-dissolving minerals** such as calcite, apatite or iron hydroxides, the metal is released as acid dissolves the grain from the outside in. In **slow-dissolving minerals** such as aluminosilicate glass, the acid must diffuse through a leached outer layer before it reaches fresh material. The **locked** fraction sits in phases that no recipe in the tested range releases. The shares of the four hosts add up to one.

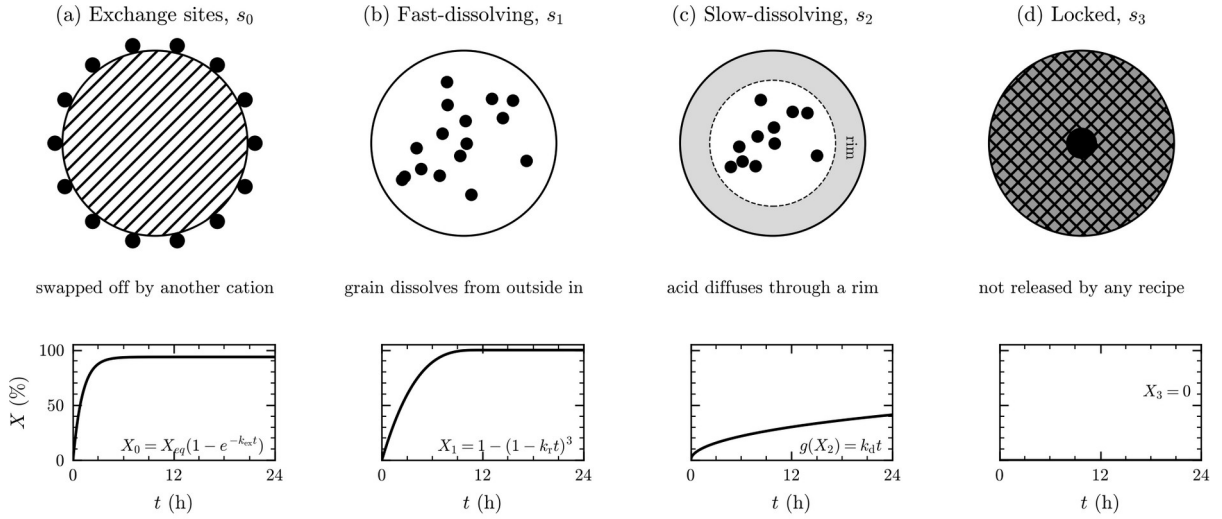


Figure 2. The four metal hosts (a to d) and their conversion $X(t)$ at one recipe (0.5 mol L^{-1} acid, 40°C , $r = 0.05 \text{ mm}$). Black dots mark the metal. Hatching marks a clay or oxide grain in (a) and a resistant phase in (d); the grey ring in (c) is the leached rim. Exchange is fast and levels off at an equilibrium. A fast-dissolving grain is consumed in hours. A slow-dissolving grain releases metal as the square root of time at first. The locked share releases nothing.

Each host has a conversion $X(t)$, the fraction of its metal released by time t . Recovery is the share-weighted sum,

$$R(t) = s_0 X_0(t) + s_1 X_1(t) + s_2 X_2(t), \quad s_0 + s_1 + s_2 + s_3 = 1, \quad (1)$$

where R is the fraction of the metal in solution, and s_0 to s_3 are the shares on exchange sites, in fast-dissolving minerals, in slow-dissolving minerals and in the locked fraction.

Exchange approaches a Langmuir equilibrium at a first-order rate,

$$X_0 = \frac{Ka}{1+Ka}(1 - e^{-k_{\text{ex}}t}), \quad (2)$$

where a is the effective concentration of the driving ion (mol L^{-1} , Eqs. 5 and 6), K is the exchange affinity (L mol^{-1}) and k_{ex} is the exchange rate constant (h^{-1}).

A fast-dissolving grain shrinks at a rate set by the surface reaction (Levenspiel, 1999),

$$X_1 = 1 - (1 - \min(k_r t, 1))^3, \quad (3)$$

where k_r is the inverse of the time needed to dissolve the grain completely (h^{-1}).

A slow-dissolving grain is controlled by diffusion through its leached layer (Levenspiel, 1999), and its conversion is the root of

$$1 - 3(1 - X_2)^{2/3} + 2(1 - X_2) = k_d t, \quad (4)$$

where k_d is the diffusion rate constant (h^{-1}). With $w = 1 - (1 - X_2)^{1/3}$ the equation becomes the cubic $w^2(3 - 2w) = k_d t$, whose form avoids round-off for small $k_d t$. LixaLearn finds its root with 30 Newton steps, which are differentiable, so gradients pass through the solve during training.

2.2 How the recipe enters

The recipe changes only the three rate constants and the exchange equilibrium. The dose of driving ions left after carbonate minerals have consumed their share on contact is

$$q = \max\left(C n_{\text{ion}} - \delta_{\text{acid}} \frac{c_{\text{carb}}}{L/S}, 10^{-4} \text{ mol L}^{-1}\right), \quad (5)$$

where C is the reagent concentration (mol L^{-1}), n_{ion} is the number of driving ions per mole of reagent (three for citric acid, two for sulfuric acid and ammonium sulfate, one otherwise), δ_{acid} is one for an acid and zero for a salt, c_{carb} is the number of driving ions consumed by carbonates per kilogram of solid (mol kg^{-1}) and L/S is the liquid-to-solid ratio (L kg^{-1}). In the code the floor is smooth (a softplus), so that the gradient with respect to c_{carb} does not vanish on acid-starved runs. For a strong acid or a salt the effective concentration is $a = q$. Citric acid is weak: its capacity is three protons per mole, but only a small part of them is free at any time. Its effective concentration is the free proton concentration of the acid that is left, from the first dissociation,

$$a = \frac{1}{2} \left(-K_a + \sqrt{K_a^2 + 4K_a q/n_{\text{ion}}} \right), \quad (6)$$

where $K_a = 10^{-3.13} \text{ mol L}^{-1}$ is the first dissociation constant of citric acid at 25 °C. Complexation of rare earths by citrate is ignored. The two dissolving hosts use $a_{\text{dis}} = \delta_{\text{acid}} a$, which is zero for a salt: a salt swaps metal off exchange sites but dissolves nothing.

Very fine grains do not dissolve without limit as they get smaller: below some size the rate is set by the surface chemistry and the solution, not by the grain size. LixaLearn therefore uses an effective radius

$$r_{\text{eff}} = \sqrt{r^2 + r_c^2}, \quad (7)$$

where r is the particle radius and r_c is a critical radius learned for each feedstock (both in mm). For r much larger than r_c the effective radius is the particle radius; for r much smaller it levels off at r_c . Temperature T and effective radius enter the rate constants through

$$k_{\text{ex}} = k_{\text{ex},0} r_{\text{eff}}^{-1/2} A(15 \text{ kJ mol}^{-1}), \quad (8)$$

$$k_r = k_{r,0} a_{\text{dis}}^n r_{\text{eff}}^{-1} A(E_a), \quad (9)$$

$$k_d = k_{d,0} a_{\text{dis}}^{-2} r_{\text{eff}}^{-2} A(E_a/2), \quad (10)$$

where n is the reaction order with respect to the driving ion and E_a is the activation energy of dissolution (kJ mol^{-1}). The constants $k_{\text{ex},0}$, $k_{r,0}$ and $k_{d,0}$ are the values at $r_{\text{eff}} = 1 \text{ mm}$ and 25°C , the latter two also at $a_{\text{dis}} = 1 \text{ mol L}^{-1}$; $k_{r,0}$ has units of $\text{h}^{-1} (\text{mol L}^{-1})^{-n}$ and $k_{d,0}$ of $\text{h}^{-1} (\text{mol L}^{-1})^{-1}$. Surface reaction scales with the inverse radius and diffusion through a shell with the inverse square (Levenspiel, 1999). The exchange rate is given a weak empirical radius dependence, $r_{\text{eff}}^{-1/2}$, and diffusion uses half the dissolution activation energy; both are modelling choices of this work. The Arrhenius factor is

$$A(E) = \exp\left[-\frac{E}{R_g}\left(\frac{1}{T} - \frac{1}{298.15 \text{ K}}\right)\right], \quad (11)$$

where R_g is the gas constant and T is in kelvin.

Together with the five numbers introduced in Sect. 2.3, a feedstock is thus described by 17 numbers: four shares, $k_{\text{ex},0}$, K , $k_{r,0}$, n , E_a , $k_{d,0}$, c_{carb} , r_c , ϕ , K_{sp} , β , ΔH_{sol} and m . Given these, Eqs. (1) to (12) give the recovery curve for any recipe. The curves rise with time and stay between 0 and 1, so the model cannot follow a recovery that falls with time.

2.3 Hosts limited by solubility

Some fast-dissolving minerals do not dissolve completely, because the liquid becomes saturated first. In phosphogypsum the rare earths sit in gypsum, and they are released only as far as gypsum dissolves (Li et al., 2022; Li, 2024). LixaLearn therefore lets a part ϕ of the fast-dissolving host follow the same rate law but stop at the solubility of its mineral. The recovery from the fast host becomes $s_l[(1 - \phi) X_l + \phi X_{ls}]$, with

$$X_{ls} = \min\left(X_l, \frac{(L/S)S}{m}\right), \quad S(S + c_s) = K_{\text{sp}}(1 + \beta h)A(\Delta H_{\text{sol}}), \quad (12)$$

where S is the solubility of the host mineral (mol L^{-1}), m is the amount of that mineral per kilogram of solid (mol kg^{-1}), c_s is the sulfate concentration brought by the reagent (mol L^{-1} ; C for sulfuric acid and the sulfate salts, zero otherwise), K_{sp} is a conditional solubility product in water ($\text{mol}^2 \text{ L}^{-2}$), h is the free acid concentration ($h = a_{\text{dis}}$), β (L mol^{-1}) is the rise of solubility with acid and ΔH_{sol} is the enthalpy that sets its change with temperature. The left side of the second equation is the common-ion effect: sulfate in the reagent lowers the solubility of a sulfate mineral. The term $1 + \beta h$ represents acid that converts sulfate to bisulfate and so raises the solubility. In the code the minimum is smooth. For $\phi = 0$, Eqs. (1) to (11) are recovered.

Some tests hold the pH at a set value by adding acid, for example a salt solution kept at pH 3. For such runs the dissolving hosts see a free acid concentration of at least $10^{-\text{pH}} \text{ mol L}^{-1}$, so that $a_{\text{dis}} = \max(\delta_{\text{acid}}, 10^{-\text{pH}})$. The same input is given to the comparison methods.

2.4 From bulk chemistry to rate-law parameters

A neural network maps the description of a feedstock to its 17 parameters. The input is the CaO , SiO_2 , Al_2O_3 and Fe_2O_3 content in weight percent, the logarithm of the rare earth grade, and a one-hot code for the feedstock type. The numeric inputs are standardised with the mean and standard deviation of the training feedstocks. The network has two hidden layers of 64 units with SiLU activation. Its output z is unconstrained and is mapped to physical values. A softmax gives the four shares. Exponentials give K , the three rate constants, c_{carb} , r_c , K_{sp} , β and m ; logistic functions give ϕ and ΔH_{sol} (-40 to 40 kJ mol^{-1}). Logistic functions keep n between 0.3 and 1.5 and E_a between 10 and 80 kJ mol^{-1} . The final layer starts with small weights and a bias equal to a neutral feedstock with equal shares and $r_c = 0.01 \text{ mm}$.

The network never predicts recovery directly. Its output passes through Eqs. (1) to (12), and the loss compares the resulting curves with the measured curves,

$$\mathcal{L}(\theta) = \frac{1}{N} \sum_j w_j \sum_t [R(t; g_\theta(\mathbf{x}_{m(j)}), \text{recipe}_j) - y_j(t)]^2, \quad (13)$$

where θ are the network weights, w_j is the weight of run j (Sect. 2.7), g_θ is the network, $\mathbf{x}_m$ is the description of feedstock m , run j used feedstock $m(j)$, recipe_j is the reagent, C , T , r and L/S of run j , $y_j(t)$ is the measured recovery of run j at time t and N is the weighted number of measured points. Training uses Adam (Kingma and Ba, 2015) with a learning rate of 3×10^{-3} , weight decay of 10^{-4} , a cosine schedule, gradient clipping at 5 and 1500 full-batch epochs. Five networks are trained from different random starts (Lakshminarayanan et al., 2017).

2.5 Update from a few test runs

For a new feedstock, each network gives a first guess $\mathbf{z}_{\text{prior}}$. The k test runs on that feedstock then update the guess. The update minimises the misfit to the test runs plus a penalty for moving away from the guess,

$$\mathbf{z}^* = \arg \min_{\mathbf{z}} \frac{1}{N_k} \sum_{\text{test runs}} \sum_t (R(t; \mathbf{z}) - y(t))^2 + \frac{\lambda}{17} \sum_{i=1}^{17} \left(\frac{z_i - z_{\text{prior},i}}{\sigma_i} \right)^2, \quad (14)$$

where N_k is the number of measured points in the test runs, $\lambda = 0.01$ is the weight of the penalty and σ_i is the spread of parameter i across the five networks, with a floor of 0.5. The update runs 300 Adam steps with a learning rate of 0.05 for each network. Only the 17 parameters of the new feedstock change; the network weights stay fixed. With no test runs, $\mathbf{z}^*$ is the network's guess. The update is a maximum a posteriori estimate with the ensemble as prior, related to the hierarchical-Bayes view of few-shot learning (Grant et al., 2018). The settings λ , the σ floor and the step count were set by hand during development on the synthetic data; no separate validation split was used to choose them. In practice the spread exceeded the floor for only 52 % of the parameters, so the penalty is close to uniform.

2.6 Feedstocks outside the training data

A guess made far from the training data can be confidently wrong, and the penalty of Eq. (14) then holds the update close to it. Before the update, LixaLearn therefore checks every input against the training data. The bulk chemistry and grade are compared with the range of the training feedstocks of the same type, and the temperature, particle radius, liquid-to-solid ratio and the concentration of each reagent with the range of all training runs. If any input lies outside its range, every σ_i is raised to at least 2, the value used by the physics-only model (Sect. 2.13). The guess is then only a starting point, and the test runs can overrule it. With no test runs the check changes nothing, but it is reported, so that the user knows the guess is an extrapolation.

2.7 Training on measured runs

Synthetic curves teach the network the structure of the problem; measured curves tie it to real feedstocks. Measured runs can be added to the training data next to the synthetic ones. A measured run usually has one point and a synthetic run seven, so each measured run is given a weight $w_j = 50$ in Eq. (13), and $w_j = 1$ otherwise. With this weight, 20 measured runs count about as much as the 25 synthetic

feedstocks of one type. The same rows, with the same weight, are given to the comparison methods (Sect. 2.13).

2.8 Error band

The spread of the five networks measures how unsure they are about the parameters. It does not measure how well the four-host model can describe a curve. A second term covers that: the root-mean-square misfit Δ of the ensemble on its own training feedstocks. The predicted standard deviation is

$$s_{\text{pred}} = \sqrt{\text{sd}_{\text{ens}}^2 + \Delta^2}, \quad (15)$$

where sd_{ens} is the standard deviation of the five predictions. The 95 % band is the mean prediction $\pm 1.96 s_{\text{pred}}$.

2.9 Ranking recipes

Once a feedstock has been learned, recovery can be predicted for any candidate recipe, and the candidates can be ranked by predicted recovery at a chosen contact time. Cost, effluent limits and scale-up are not part of LixaLearn.

2.10 Pore-scale transport

The four-host model treats the solid as a stirred suspension. In a packed column the leaching liquid must first reach the grains. To show this effect, LixaLearn includes a transport model on two-dimensional images of grain packings. A lattice Boltzmann solver from Lixa gives the steady water velocity $\mathbf{u}$ in every pore pixel at a fixed driving force (Krüger et al., 2017). The leaching agent c_A then follows

$$\frac{\partial c_A}{\partial t} + \mathbf{u} \cdot \nabla c_A = D \nabla^2 c_A, \quad (16)$$

where c_A is the agent concentration scaled by its inlet value and D is the diffusion coefficient. The dissolved metal M and the metal still held on the grain surface I follow

$$\frac{\partial M}{\partial t} + \mathbf{u} \cdot \nabla M = D \nabla^2 M + k_{\text{rel}} c_A I, \quad \frac{\partial I}{\partial t} = -k_{\text{rel}} c_A I, \quad (17)$$

where k_{rel} is the release rate constant. The metal starts on the pore pixels that touch a grain, and no flux enters the grains. The agent enters at the left edge, and the metal is collected at the right edge. Velocities are scaled by the mean pore speed of the open packing, so two packings driven at the same pressure share one time scale. Time is counted in flushes, the time for water at that speed to cross the image once. The Péclet number $\text{Pe} = \bar{u}L/D = 50$ compares flow with diffusion, and the Damköhler number $\text{Da} = k_{\text{rel}} L/\bar{u} = 3$ compares release with flow, where $\bar{u}$ is the mean pore speed of the open packing and L the image width. The face fluxes are made exactly divergence-free by a discrete projection on the pore graph, and the equations are solved with first-order upwind advection, five-point diffusion and an explicit time step that keeps the scheme bounded. Unit tests confirm that metal is conserved to round-off and that c_A stays between 0 and 1 without clipping.

2.11 Synthetic benchmark

The benchmark has 25 synthetic feedstocks for each of seven types: weathered ion-adsorption clay, low-calcium and high-calcium coal fly ash, coal refuse, mine-water treatment sludge, red mud and

phosphogypsum. **All benchmark data are synthetic.** The bulk chemistry of each feedstock is drawn at random within broad ranges for its type (Appendix B). A set of hidden rules then turns the chemistry into the true host shares, rates and carbonate content; for example, the exchange share of a clay rises with its alumina content. These rules are not given to the learner. The reference model uses the same four hosts, the same acid balance, the same weak-acid treatment of citric acid and the same form of critical radius as the learner (with r_c drawn between 0.01 and 0.03 mm). In phosphogypsum, and in some mine-water sludges and high-calcium ashes, part of the fast host sits in gypsum or anhydrite, and the reference model caps its dissolution at a solubility computed from the gypsum solubility product with bisulfate formation (whose constant falls with temperature) and an ionic-strength correction, a richer form than the learner's Eq. (12). The benchmark therefore tests whether the learner can find the parameters of a structure close to its own, not whether that structure is right; the real data test the latter.

Each feedstock was leached with 6 random recipes (Appendix B). The recipe ranges were set to cover the conditions of published bench tests, including grains down to 1 μm , liquid-to-solid ratios up to 50 L kg^{-1} , acid up to 2.5 mol L^{-1} and temperatures from 10 to 90 $^{\circ}\text{C}$. Clays could take a salt or an acid; the other types took sulfuric, hydrochloric, nitric or citric acid. Most acid recipes were dosed above the carbonate demand, and 15 % were deliberately starved of acid. Recovery was read at 7 times from 0.25 to 24 h, and Gaussian noise with a standard deviation of 2 percentage points was added. The benchmark has 175 feedstocks, 1050 runs and 7350 points.

The curves come from the batch reactor of Lixa (Asgari, 2026), which integrates the reagent balance in time. In that model acid is consumed by the metal-bearing minerals and by slow silicate dissolution, the reagent is depleted as the run proceeds, and the fast-dissolving host has mixed reaction and diffusion control; the full equations are given by Asgari (2026). The learner's laws assume a constant effective concentration and pure control. In 14 of the 1050 runs the noise-free recovery fell by more than 5 points between 8 and 24 h, which the learner cannot reproduce. The learner therefore cannot reach zero error even with perfect parameters.

2.12 Real data

Three published datasets were used. Two shaped the model and are development sets; the third was kept apart and used once, as the test. The history matters for reading the results, so it is given here in full.

Red mud (development). Ray et al. (2025) leached red mud with citric acid in a central composite design of 20 runs. The factors were concentration (0.32 to 2.43 mol L^{-1}), temperature (283 to 358 K) and time (39 to 291 min), at a liquid-to-solid ratio of 50 L kg^{-1} and a median particle size of 3.74 μm . The total rare earth leaching efficiency of each run was taken from their Table 4. Six runs repeat the centre point. The article gives typical red mud ranges but no bulk analysis of its own sample, so the midpoints of those ranges were used (51 % Fe_2O_3 , 18.5 % Al_2O_3 , 5 % SiO_2 , 1.5 % CaO), and the grade was set to the median of the synthetic red mud. A first version of LixaLearn (v0.1) failed on these data. The critical radius, the weak-acid treatment, the wider recipe ranges, the out-of-range check and the training on measured runs (Sects. 2.2, 2.6 and 2.7) were added after that failure (v0.2).

Phosphogypsum (pre-registered test of v0.2, then development). Li et al. (2022) leached phosphogypsum with hydrochloric, nitric and sulfuric acid. Their supporting tables give 57 runs (19 per acid) at 0.5 to 2.5 mol L^{-1} , 45 to 85 $^{\circ}\text{C}$ and liquid-to-solid ratios of 10 to 30 L kg^{-1} . The contact time (20 min, on the plateau of recovery) and the particle size (about 10 to 20 μm by electron microscopy, used as a

radius of 7.5 μm) were taken from the doctoral thesis of the first author (Li, 2024). The recovery of each run is the grade-weighted mean of the reported Nd, Y and Dy recoveries. The bulk chemistry is 35.4 % CaO, 0.11 % Al_2O_3 and 0.09 % Fe_2O_3 , with a total rare earth grade of 295 ppm; SiO_2 is not reported and was set to the median of the synthetic phosphogypsum. These data were first used as a held-out test of v0.2, with the protocol written and the code frozen beforehand, and v0.2 failed it. The solubility-limited host of Sect. 2.3 and gypsum-bearing synthetic feedstocks were added after that failure (v0.3), so the phosphogypsum data are a development set for v0.3.

Ion-adsorption clay (held-out test of v0.3). Anawati (2022) desorbed rare earths from an ion-adsorption clay with ammonium sulfate in a central composite design of 29 runs: 0.15 to 1.0 mol L^{-1} , 25 to 45 $^\circ\text{C}$, liquid-to-solid ratios of 2 to 4 L kg^{-1} and pH 2 to 4, held by adding sulfuric acid, with 20 min of contact (Table 6.1 and Appendix Table 14.1 of the thesis). Recovery is the grade-weighted first-contact extraction of Sc, Y and the lanthanides. The inputs were 0.07 % CaO, 15.1 % Al_2O_3 and 21.0 % Fe_2O_3 (an aqua regia digest, so lower bounds), SiO_2 set to the median of the synthetic clays, a grade of 3672 ppm and a radius of 0.5 mm (from a sieve analysis). The protocol was written and v0.3 frozen (a version-control commit) before any model saw these data. The set-pH input of Sect. 2.3 was added at that stage, from the description of the experiments, not from their results. The data were transcribed with the help of an AI assistant, whose summary mentioned the range of recovery before the protocol was written; no model output was seen. All methods were trained on the 175 synthetic feedstocks plus the 77 runs of the two development sets, weighted as in Sect. 2.7. The criterion of success, set in advance, was that after three test runs LixaLearn has a lower MAE than gradient boosting, the direct network and the mean of the test runs.

For all three datasets each run is a single point at one time, so k real test runs carry k points, while a synthetic test run carries seven. $k = 1$ used every run once as the test run; $k = 3$ and 5 used the same 50 random draws for every method, and the remaining runs were scored. For the two development sets, the models were trained on the synthetic feedstocks plus, for phosphogypsum, the red mud runs.

2.13 Comparison methods and scores

Three methods were compared with LixaLearn. **Gradient boosting (GB)** maps the feedstock description, a one-hot code for the reagent, the logarithms of concentration, particle radius, liquid-to-solid ratio and time, the temperature, and the two dose terms of Eq. (5) (driving ions per litre and per kilogram of solid) straight to recovery (HistGradientBoostingRegressor in scikit-learn; Pedregosa et al., 2011; Ke et al., 2017). Recovery is constrained to rise with time. The number of trees (200, 400, 800), learning rate (0.05, 0.1) and leaves per tree (15, 31) were chosen by three-fold cross-validation grouped by feedstock on the training feedstocks of each fold. The **direct network (NN)** has the same size as LixaLearn's network but predicts recovery directly from the same inputs as GB, with no rate laws. For k test runs, GB and NN are refitted with the test runs added and weighted ten times. The **physics-only** model uses the rate laws and the update of Eq. (14), but starts from the mean network output over the training feedstocks of the same type, with $\sigma = 2$. It has the physics and the feedstock type, but no feedstock-specific guess.

The synthetic feedstocks were split into five folds, with each type spread evenly. Each fold in turn served as the unseen feedstocks while the other four trained the models. The six runs of every unseen feedstock were put in a fixed random order; the first k runs ($k = 0$ to 3) were the test runs and the last three runs were always the ones scored. The score is the mean absolute error (MAE) over all scored points, in percentage points of recovery (points). The assay noise alone gives an MAE of 1.56 points. Differences between methods are tested per feedstock with the Wilcoxon signed-rank test.

3 Results

3.1 The benchmark

Figure 3 shows the benchmark. Most feedstock types separate in composition, mainly along their calcium and iron contents, while clay, low-calcium ash and coal refuse overlap. The mean noise-free recovery after 24 h ranged from 16 % for coal refuse to 86 % for mine-water sludge. 26 runs had a noise-free recovery below 2 % after 24 h, and 73 % of these were dosed with less acid than the carbonate could consume. Because the recipe ranges are wide, 42 % of the unseen feedstocks had at least one input outside the range of their training folds, and their update was loosened (Sect. 2.6).

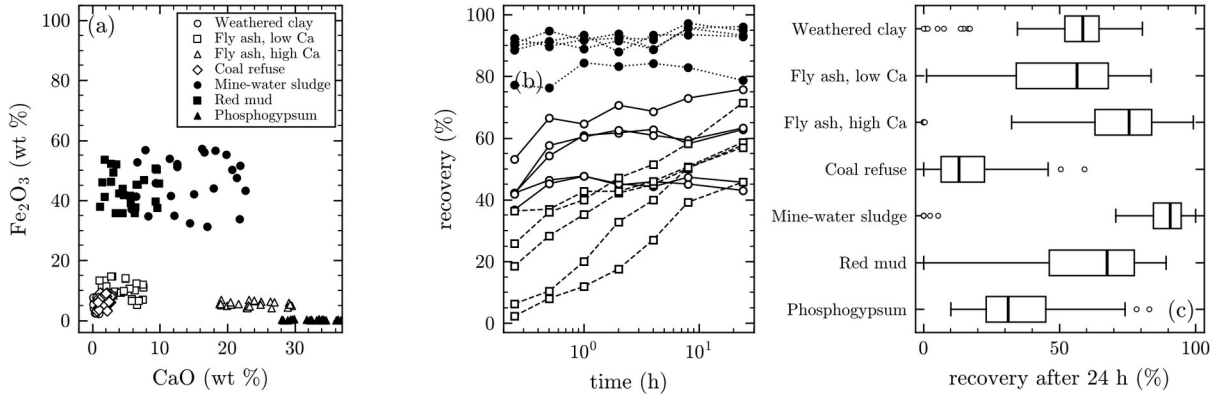


Figure 3. The synthetic benchmark. (a) CaO and Fe₂O₃ content of the 175 feedstocks. (b) Five example runs for each of three types: weathered clay (solid lines, open circles), low-calcium fly ash (dashed, open squares) and mine-water sludge (dotted, filled circles); time on a logarithmic axis. Runs near zero were starved of acid. (c) Recovery after 24 h over all runs of each type; boxes show the quartiles and the median, whiskers 1.5 times the interquartile range, and circles the outliers.

3.2 Prediction error for unseen feedstocks

Table 1 and Fig. 4 give the main result. With no test runs, the direct network had the lowest error (6.4 points), against 6.6 for LixaLearn, 7.0 for the physics-only model and 7.5 for GB; LixaLearn and NN did not differ for a typical feedstock ($p = 0.32$). One test run lowered the LixaLearn error to 6.0 points and three to 5.4. GB and NN improved more slowly, to 6.7 and 5.7 points after three test runs. After three test runs LixaLearn had a lower error than GB for 68 % of the feedstocks ($p < 0.0001$) and lower than NN for 58 % ($p = 0.01$). After one test run the difference from NN was not significant ($p = 0.25$). The rate laws therefore help most when test runs are available: they carry what a test run shows about the feedstock to other recipes.

Table 1. Mean absolute error (points) on the last three runs of each of the 175 unseen synthetic feedstocks, with 95 % confidence intervals of the mean over feedstocks; five-fold cross-validation. The last column scores LixaLearn against the curves before noise was added.

Test runs k	LixaLearn	Physics only	Gradient boosting	Direct network	LixaLearn, noise-free
0	6.57 ± 0.76	6.99 ± 0.81	7.45 ± 0.86	6.37 ± 0.65	6.32
1	5.99 ± 0.73	6.52 ± 0.81	7.11 ± 0.79	6.03 ± 0.58	5.68
2	5.47 ± 0.73	5.89 ± 0.79	6.62 ± 0.72	5.85 ± 0.57	5.17
3	5.37 ± 0.75	5.41 ± 0.72	6.68 ± 0.72	5.67 ± 0.56	5.02

The physics-only model shows what the network adds. LixaLearn had a lower error than the physics-only model for 56 % of feedstocks with no test runs ($p = 0.008$), 61 % after one ($p < 0.001$) and 61 % after three ($p = 0.02$). The means after three test runs were close (5.4 against 5.4 points), and by type the physics-only model was worse mainly for phosphogypsum (4.3 against 3.7 points) and red mud (7.2 against 6.3) and better for high-calcium fly ash (5.5 against 6.7). On the synthetic data the feedstock-specific guess therefore adds a little; most of the gain over GB and NN comes from the rate laws.

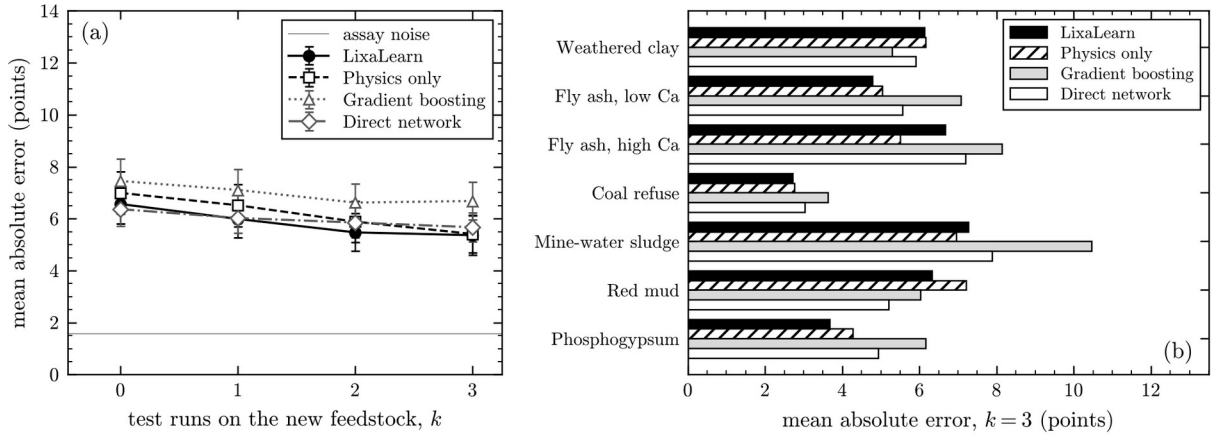


Figure 4. Prediction error for unseen synthetic feedstocks. (a) Mean absolute error on unseen recipes against the number of test runs k on the new feedstock. Error bars are 95 % confidence intervals of the mean over the 175 feedstocks. The thin grey line is the error that assay noise alone gives. (b) Error after three test runs by feedstock type.

By type (Fig. 4b), LixaLearn had the lowest error after three test runs, or was within 0.05 points of it, for three of the seven types. For weathered clay, GB was better (5.3 against 6.1 points). For high-calcium fly ash, the physics-only model was better (5.5 against 6.7 points). For mine-water sludge, the physics-only model was better (7.0 against 7.3 points). For red mud, NN was better (5.2 against 6.3 points). After three test runs the error was 5.4 points, 3.4 times the noise level. Scored against the noise-free curves, it was 5.0 points. This remaining error is model mismatch: the closed-form laws cannot follow reagent depletion and mixed control.

Figure 5 shows three unseen feedstocks. With no test runs, the predicted curves of the clay lay close to the measured points. For the clay, one recipe whose recovery fell slightly with time was predicted about 15 to 20 points too high, before and after three test runs, because the rate laws cannot follow a falling curve. For the low-calcium ash, the guess was close, and three test runs on other recipes brought the curves onto the points (Appendix A). For the red mud, the slowest recipe was predicted well, while the plateau of the fastest stayed about 8 points too low.

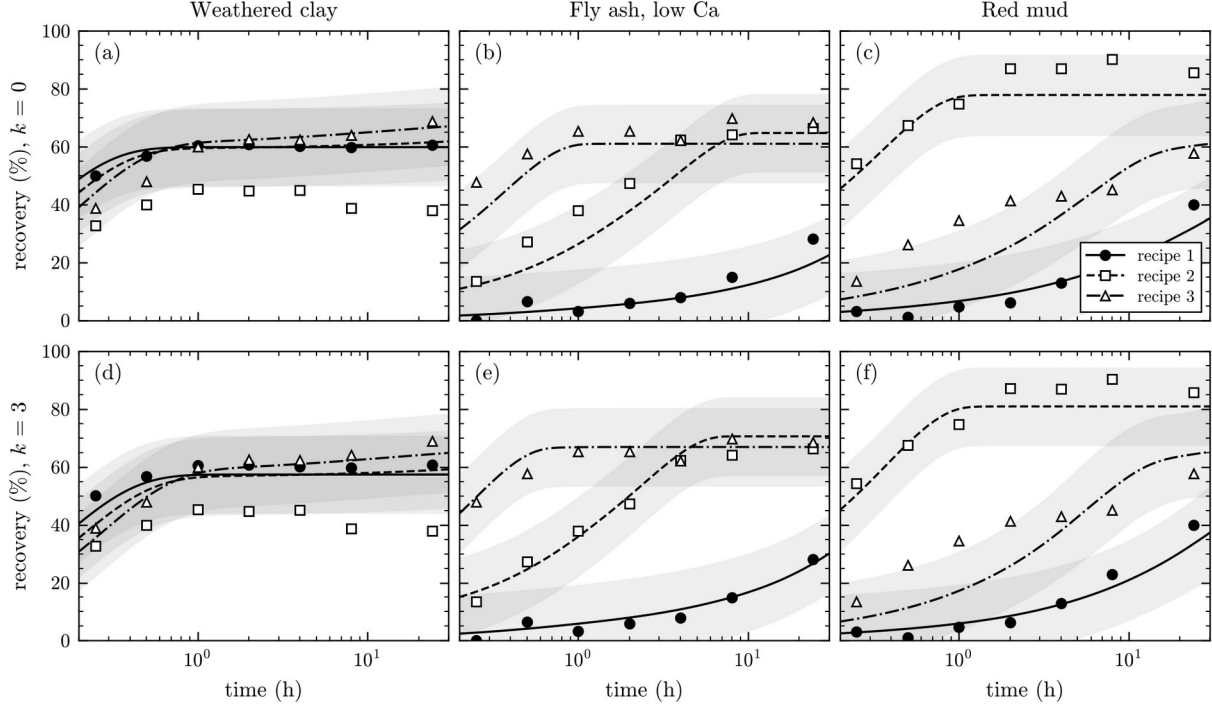


Figure 5. Three unseen synthetic feedstocks, one per column. Line styles and markers distinguish three recipes the model was not shown; markers are measured points, lines the LixaLearn predictions and grey bands the 95 % error bands (the bands of different recipes overlap). Top row (a to c): no test runs. Bottom row (d to f): after three test runs on other recipes. Time is on a logarithmic axis.

3.3 Host shares

Because the network outputs physical parameters, its shares can be compared with the true shares of the synthetic feedstocks (Fig. 6). Two shares were recovered: the exchange share (correlation 0.82, MAE 13.4 points with no test runs) and the locked share (0.89, 5.8 points). The locked share is close to recovery by construction, since it is one minus the plateau of the curves, and much of both correlations comes from differences between types. The fast- and slow-dissolving shares were poorly recovered: their errors were 20 and 22 points and their correlations with the truth 0.31 and -0.34. Three test runs changed this little (18 and 22 points). Within the sampled recipes and the 24 h window, a fast host with a slow rate and a slow host with a fast rate give nearly the same curves, so recovery can be predicted although the split between the two is wrong.

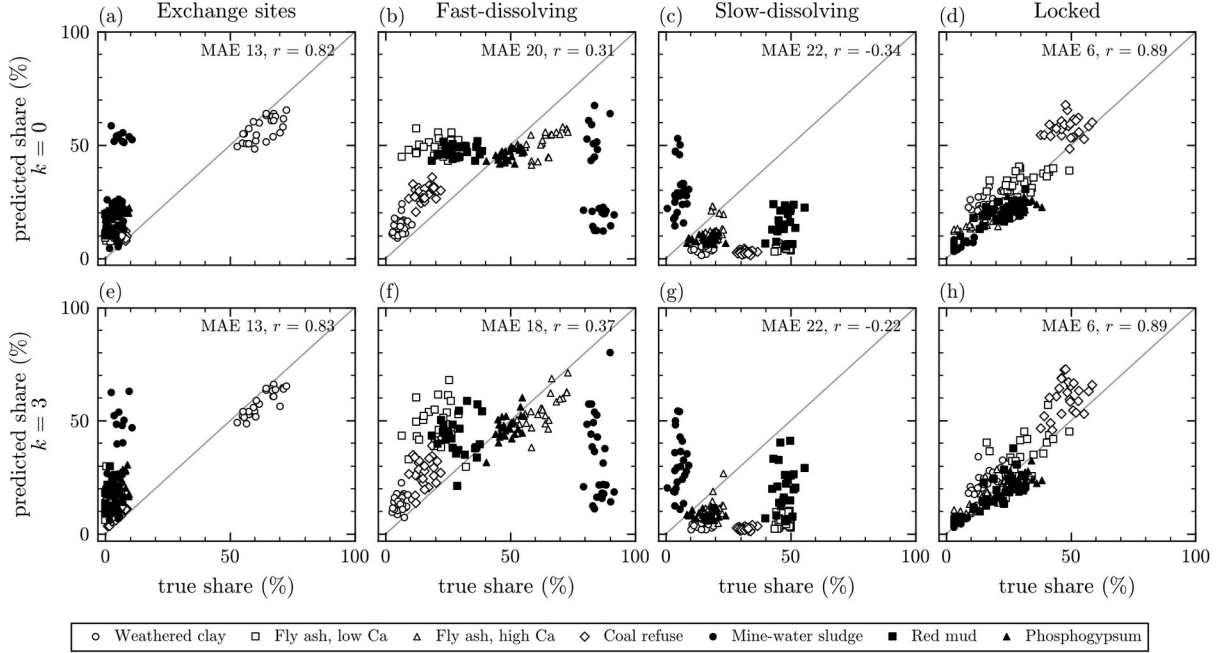


Figure 6. Predicted against true host shares for the unseen synthetic feedstocks, with no test runs (a to d) and after three test runs (e to h). Each marker is one feedstock; marker shapes identify the type. The grey diagonal marks perfect agreement.

3.4 Error band

The spread of the five networks alone was small (on average 1.3 points). Bands built from that spread plus the assay noise covered only 51 % of the measured points with no test runs and 63 % after three, against a target of 95 %. Adding the training misfit $\Delta = 7.0$ points (Eq. 15) gave 91 % with no test runs and 94 % after three. Because Δ dominates, the band is nearly the same for every prediction (about ± 14 points). It is calibrated on average but says little about which predictions are more uncertain. After three test runs, coverage by type ranged from 91 to 99 %.

3.5 Ranking recipes

For each of the 35 unseen feedstocks in the first fold, 12 candidate recipes were ranked by their predicted recovery at 8 h after three test runs (Fig. 7). The candidates were drawn with the benchmark's recipe generator, using the median carbonate of the training feedstocks of the same type to set the doses, and their true recovery was computed with the reference model. LixaLearn's predictions differed from the truth by 5.6 points on average, against 6.4 (physics only), 6.5 (GB) and 5.6 points (NN). Its median rank correlation within a feedstock was 0.92, against 0.87 for GB and 0.88 for NN, and its top recipe was the true best for 19 of 35 feedstocks (GB 20, NN 16). Its top recipe was within 5 points of the best for 32 feedstocks (physics only 32, GB 32, NN 31), and on average it gave up 1.3 points against the best of the 12, against 1.1 (physics only), 1.1 (GB) and 1.6 points (NN). A random pick gave up 19.4 points. All four methods therefore pick a good recipe, and none is clearly best at it. Of the 420 LixaLearn predictions, 20 were off by more than 20 points (7 for high-calcium fly ash, 5 for mine-water sludge, 4 for low-calcium fly ash, 4 for red mud).

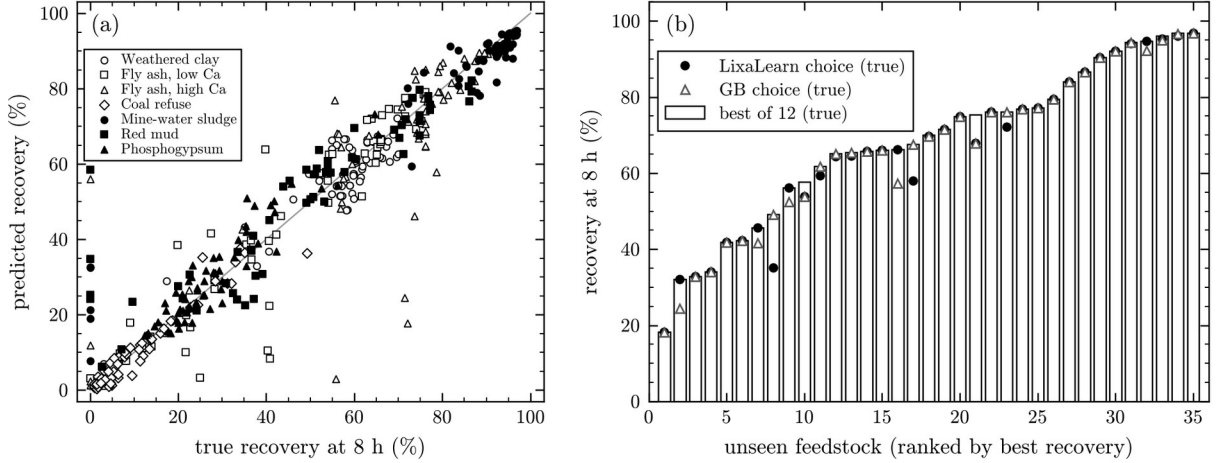


Figure 7. Ranking recipes after three test runs. (a) Predicted (LixaLearn) against true recovery at 8 h for 12 candidate recipes on each of 35 unseen synthetic feedstocks; marker shapes identify the type as in Fig. 6, and the grey line is 1:1. (b) For each feedstock, the true recovery of the best of the 12 recipes (bars), and of the recipes ranked first by LixaLearn (filled circles) and by gradient boosting (open triangles), sorted by the best value.

3.6 Development set: red mud

On the red mud (Fig. 8a), trained on synthetic feedstocks only, LixaLearn gave an MAE of 26.6 points with no test runs, against 24.1 for the physics-only model, 22.6 for GB and 26.7 for NN. Predicting every run as the mean of all 20 runs gives 12.7 points, so no method had skill without test runs. After three test runs the errors were 13.3 (LixaLearn), 13.5 (physics only), 10.1 (GB) and 8.6 points (NN), and the mean of the three test runs gave 15.7 points; after five, 12.2, 12.4, 8.8 and 7.6 points. The first version, v0.1, gave 15.2 points after three test runs and nearly flat predictions. The current model follows the recipes (Fig. 8b) and beats the mean of the test runs, but GB and NN remained better on this feedstock. Fitted to all 20 runs at once with a very weak penalty, the rate laws gave an in-sample MAE of 6.1 points and a leave-one-out MAE of 9.0 points, so the four-host structure can describe this red mud; three single-point runs were not enough to find its parameters.

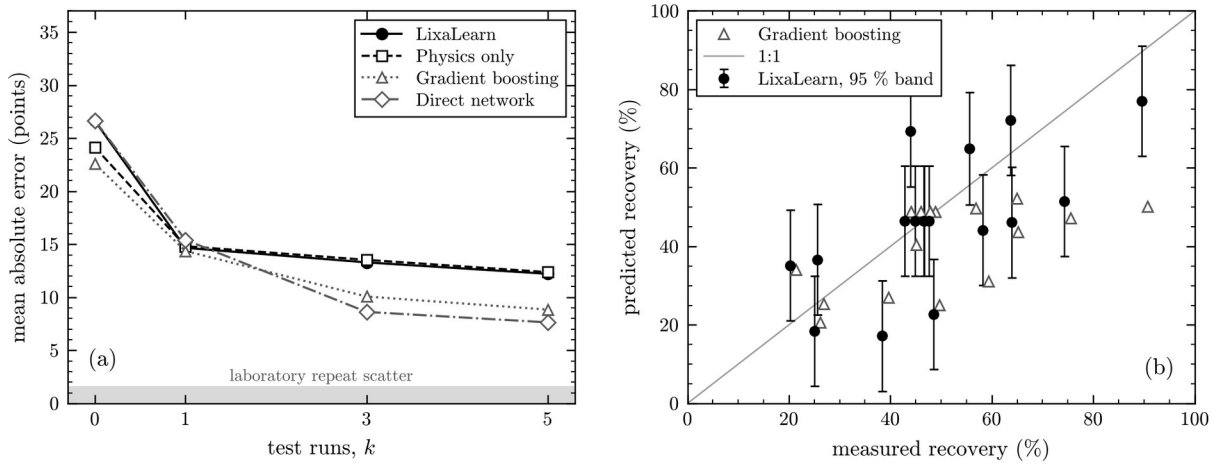


Figure 8. Development set: real red mud leached with citric acid (Ray et al., 2025), LixaLearn v0.3 trained on synthetic feedstocks only. (a) Mean absolute error on the runs not used as test runs; $k = 1$ uses every run once as the test run, $k = 3$ and 5 use the same 50 random draws for all methods, and $k = 0$ scores all 20 runs. The grey strip

is the scatter of the six repeated centre-point runs. (b) One draw with three test runs: predicted against measured recovery for the other 17 runs. Filled circles with error bars are LixaLearn with its 95 % bands, open triangles gradient boosting, and the grey line is 1:1.

3.7 Phosphogypsum: a failed test and what it taught

In its pre-registered test, v0.2 failed on the phosphogypsum. After three test runs its MAE was 16.3 points, against 15.7 for the mean of the test runs, 13.6 for GB and 14.4 for NN, and its predictions were uncorrelated with the measurements ($r = 0.00$). A diagnostic run after the test showed why. Fitted to all 57 runs at once, the four-host laws still gave an MAE of 14.0 points, and they placed sulfuric acid (fitted mean 64 %) above hydrochloric acid (62 %), while the measured means were 46 and 72 %. At 20 min the fine gypsum is on its plateau, so recovery is set by how much gypsum the liquid can hold, which sulfate suppresses; the v0.2 laws had rates but no solubility limit.

With the solubility-limited host, v0.3 described the same data well (Fig. 9). Trained on the synthetic feedstocks and the red mud, as v0.2 had been, it gave 10.6 points after one test run, 7.4 after three and 5.5 after five, against 10.9 and 11.5 points for GB and NN and 15.7 for the mean of the test runs after three. It was lower than GB in 90 % of the 50 draws and lower than NN in 88 %. Predicting each run as the mean of its own acid, which needs all the data, gives 8.7 points. The predictions now separate the acids and follow the liquid-to-solid ratio (Fig. 9b; correlation with the measurements 0.82 after three test runs). The physics-only model did as well as LixaLearn, so the gain comes from the new host, not from the network's guess. These are development results: the host was added because of these data, and they show that the structure is right for this feedstock, not that it predicts unseen ones.

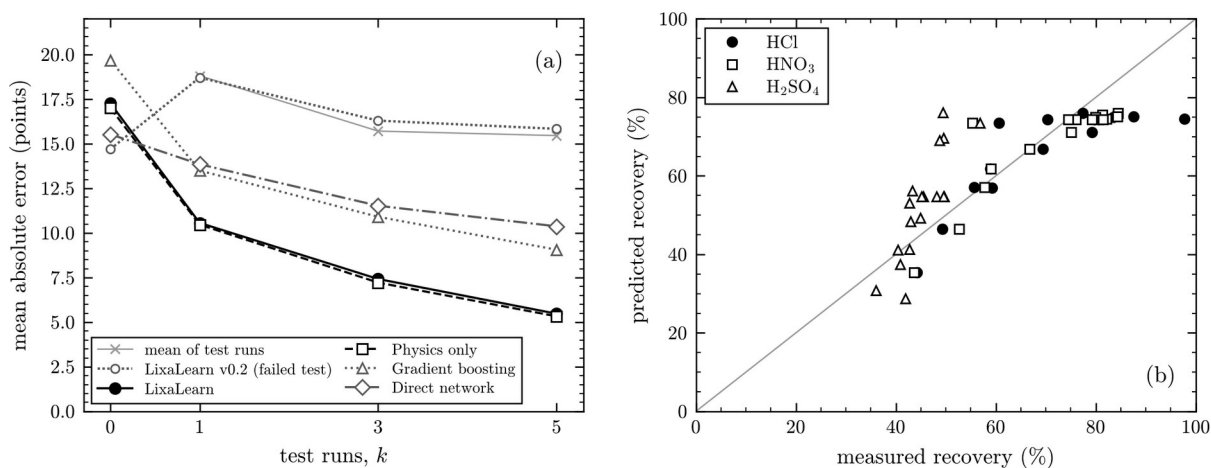


Figure 9. Phosphogypsum leached with three mineral acids (Li et al., 2022). (a) Mean absolute error on the runs not used as test runs for v0.3 (development), with the failed pre-registered test of v0.2 for comparison (dotted, open circles). (b) LixaLearn v0.3 after three test runs (one draw): predicted against measured recovery by acid; the grey line is 1:1.

3.8 Held-out test: ion-adsorption clay

The held-out clay lay outside the training data in its CaO, Al₂O₃ and Fe₂O₃ contents and grade, its ammonium sulfate concentration and its pH control, so the update was loosened. With no test runs, GB had the lowest error (5.8 points), followed by LixaLearn (7.8), NN (10.8) and the physics-only model (14.9). After three test runs the errors were 3.3 (LixaLearn), 3.2 (physics only), 5.5 (GB) and 12.3 points (NN), and

the mean of the three test runs gave 2.7 points (Fig. 10a, Table 2). LixaLearn was lower than GB in 96 % of the draws and lower than NN in 100 %, but lower than the mean of the test runs in only 20 %. The criterion set in advance was therefore not met: LixaLearn clearly beat both machine-learning models, but not the simple mean.

Table 2. Held-out test on 29 runs of an ion-adsorption clay (Anawati, 2022): mean absolute error (points) on the runs not used as test runs, with 95 % confidence intervals of the mean over draws.

Test runs k	LixaLearn	Physics only	Gradient boosting	Direct network	Mean of test runs
0	7.8	14.9	5.8	10.8	–
1	4.5 ± 0.6	4.4 ± 0.6	6.6 ± 0.2	22.4 ± 5.6	3.4 ± 0.5
3	3.3 ± 0.2	3.2 ± 0.2	5.5 ± 0.3	12.3 ± 1.4	2.7 ± 0.2
5	2.8 ± 0.2	2.9 ± 0.1	5.2 ± 0.3	7.3 ± 1.0	2.5 ± 0.1

The clay recoveries spanned only 23.8 to 38.3 %, and predicting every run as the overall mean gives 2.2 points, close to the spread of the five repeated centre-point runs (about ± 1.6 points). In such a narrow set the mean of three test runs is a strong baseline. LixaLearn matched the level of the clay after a few test runs, which GB and NN did not, but it did not rank the runs: the correlation between its predictions and the measurements was -0.03 after three test runs (Fig. 10b).

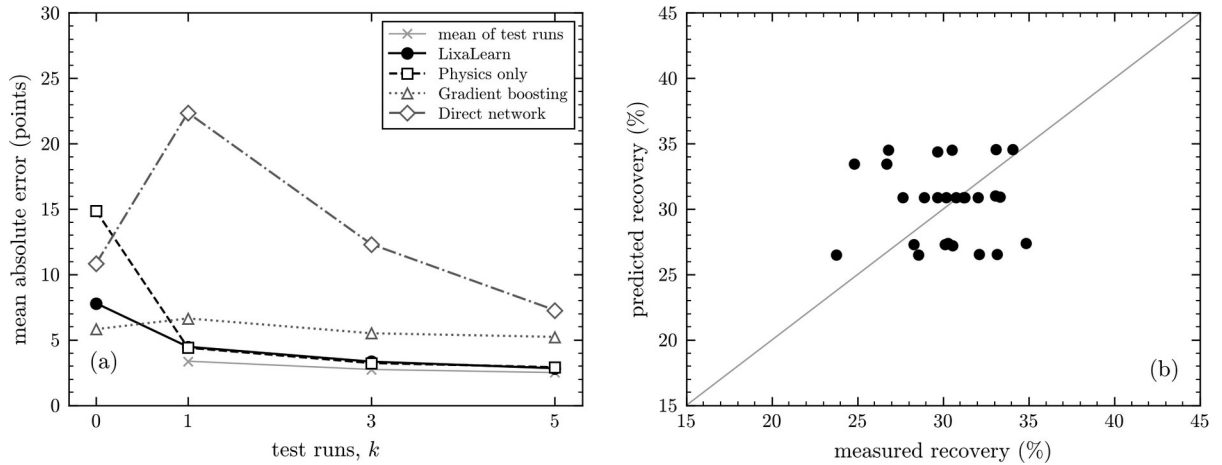


Figure 10. Held-out test: ion-adsorption clay desorbed with ammonium sulfate at a set pH (Anawati, 2022). (a) Mean absolute error on the runs not used as test runs; k = 1 uses every run once as the test run, k = 3 and 5 use the same 50 random draws for all methods, and k = 0 scores all runs. (b) LixaLearn after three test runs (one draw): predicted against measured recovery; the grey line is 1:1.

3.9 Transport through the pore space

The four-host model predicts what a stirred beaker gives. Figure 11 shows what changes when the liquid flows through a packing. The two images are synthetic grain packings: an open packing with a

porosity of 0.49 and a tight packing with a porosity of 0.39, driven at the same pressure. Water moved through the tight packing at 49 % of the mean speed in the open packing. Half of the metal had left the open packing after 1.35 flushes and the tight packing after 2.30, a ratio of 1.71. The speed ratio alone would give 2.02; diffusion carries part of the agent ahead of the flow. After two flushes, 87 % of the metal had left the open packing and 32 % the tight one, while a stirred beaker with the same release rate would release 95 % within one flush time. The same grains with the same chemistry thus give different recovery in a column, which is why recipes ranked in a beaker need a transport model such as Lixa before scale-up.

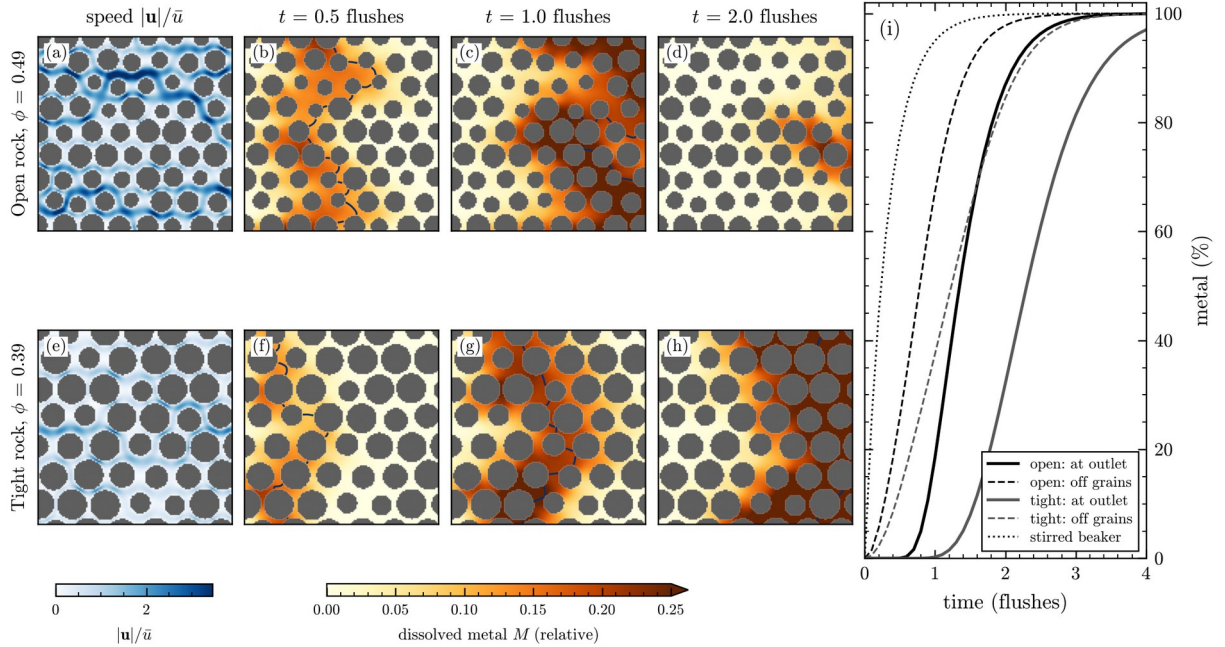


Figure 11. Pore-scale transport in an open packing (a to d) and a tight packing (e to h) driven at the same pressure. (a, e) Water speed relative to the mean pore speed of the open packing; grains are dark grey. (b to d, f to h) Dissolved metal after 0.5, 1 and 2 flushes of the open packing; the dark blue line marks where the leaching agent has reached half its inlet strength. (i) Metal released from the grains (dashed) and collected at the outlet (solid) for the open (black) and tight (grey) packing, with the stirred-beaker reference (dotted).

4 Discussion

4.1 What the rate laws and the network each add

Gradient boosting and the direct network have to learn from data that recovery stays below one, rises with time, does not respond to salts in dissolving minerals and falls when carbonate consumes the acid. LixaLearn and the physics-only model start with these facts. The comparison of the direct network with LixaLearn isolates the rate laws, because the two share a network size and see the same information. On the synthetic benchmark the rate laws did not help without test runs, but they did once test runs were available. A test run fixes the level and pace of the curve, and the rate laws carry that information to other recipes; a model without them has to learn the recipe effects from scratch for each new feedstock. The same pattern held on the real phosphogypsum and clay, where LixaLearn beat both data-driven models after one or more test runs.

The comparison of the physics-only model with LixaLearn isolates the network's guess. On the synthetic data the guess helped, most clearly with zero or one test run. On all three real feedstocks, however, the inputs lay outside the training data, the update was loosened, and the physics-only model did as well as LixaLearn. The guess is learned from synthetic feedstocks, and a real feedstock rarely looks like any of them in every respect. Nguyen et al. (2025) saw the same effect from the other side: their gradient-boosted model, trained on 572 published experiments, lost much of its accuracy on an external dataset. On real feedstocks the value of LixaLearn lies in its rate laws, which do not depend on the training data, more than in its network, which does.

The parameters are physical, but not all are identifiable from short batch tests. The model found the exchange and locked shares, which leave clear marks on the curves, and confused the two dissolving hosts, which can trade a large share at a slow rate for a small share at a fast rate. Tests designed to separate them would help: a salt test sampled in the first minutes, which releases only the exchange share, and a long acid test, which separates the slow host from the locked fraction. Until such tests are used, the dissolving shares should not be read as a mineralogical result.

4.2 Structure first, then data

The three real datasets tell a consistent story about where hybrid models gain and where they fail. A hybrid model is a bet that the mechanistic part is right in form, so that the data only need to set its parameters (Psichogios and Ungar, 1992; Willard et al., 2022). When the bet is right, few data are needed. When it is wrong, the data cannot repair it, because the model has no way to express what the data show.

The phosphogypsum shows both outcomes on the same data. Under v0.2 the rate laws had no solubility limit, and at 20 min every dissolving host had finished, so the predicted recovery was nearly the same for every recipe. Neither more training data nor more test runs could change this, and the model placed sulfuric acid, the weakest leachant for this solid, above hydrochloric acid. Under v0.3 one extra equation, the solubility of the host mineral with the common-ion effect of sulfate, let three test runs predict the other runs better than predicting each acid's own mean. Li (2024) reached the same mechanism from the experiments: rare earths in phosphogypsum follow the dissolution of the gypsum. The model did not discover this; it was told, after a failure pointed to it. The lesson is that a failed test is most useful when it says why it failed, and a diagnostic that fits the rate laws to all the runs at once does exactly that.

The red mud sits in between. Fitted to all 20 runs, the rate laws described it with a leave-one-out error of about 9 points, so the structure is adequate. Three single-point runs were not enough to pin down 17 parameters, and the guess from synthetic red mud did not supply the rest. Data that cover the time axis would help most: one run sampled at five times carries more information about the rates than five runs sampled once.

4.3 Why the clay was hard

The clay test failed in a different way. LixaLearn set the level of the clay after a few test runs, which neither data-driven model did, but it did not rank the runs, and the mean of three test runs was more accurate still. Three features of the data explain much of this. First, the recoveries were close together (24 to 38 %), so the differences between runs were only a few times the laboratory scatter, and a model has little to gain over the mean. Second, the pH was held by sulfuric acid additions whose amounts were not

reported. The set-pH input gives the dissolving hosts the right free acid, but the added sulfate and the extra acid consumed by the clay are unknown. Third, the liquid-to-solid ratios were low (2 to 4 L kg⁻¹). At such ratios the desorbed rare earths build up in the solution and compete with ammonium for the exchange sites, so the extent of exchange depends on the liquid volume (Moldoveanu and Papangelakis, 2012). The Langmuir term of Eq. (2) depends on the concentration of the driving ion only, not on how much metal is already in solution. An exchange equilibrium that includes the dissolved metal is the natural next step, and it would need to be tested on a clay dataset that was not used to motivate it.

4.4 Testing in the open

Machine learning for leaching is usually judged by random splits of a single compiled dataset, where test and training runs share feedstocks, laboratories and protocols. This study used a stricter standard: a test feedstock unseen in training, a protocol and code fixed before the test, and a single run of the test. Under that standard the method failed twice (on red mud with v0.1 and in the phosphogypsum test of v0.2) and partly passed once (on the clay with v0.3). These outcomes are reported with the same weight as the successes, because a method that is only shown where it works cannot be trusted where it has not been tried. The version history, the two protocols and the code at each step are part of the material available on request, so the path from failure to change can be checked.

The same standard shows what the results can and cannot support. The phosphogypsum result shows that the solubility-limited host describes a real feedstock well, but it is a development result. The clay result is the only clean test of v0.3, and it supports the claim that the rate laws transfer the level of a new feedstock better than data-driven models, not the claim that they rank recipes. A held-out test on phosphogypsum from another laboratory, and on a feedstock type not yet used, would be the next tests of this kind.

4.5 Uncertainty

The 95 % bands were calibrated on the synthetic data but too narrow on every real feedstock. The band combines the spread of the five networks with the training misfit Δ , and both are learned from synthetic feedstocks. On a real feedstock the misfit of the rate laws is larger, and the networks agree with each other even when they are all wrong. A band that grows with the misfit on the test runs themselves, or a misfit term estimated from the real development sets, would be more honest. Until then, the bands should be read as a lower bound on the uncertainty for real feedstocks.

4.6 Use in a laboratory

The results suggest a simple rule for using LixaLearn on a new kind of feedstock. First, fit the rate laws to a few complete runs, sampled at several times and covering contrasting recipes. If they cannot describe these runs, as for phosphogypsum under v0.2, the structure must be extended before the method is used. If they can, one to three test runs on each new sample of that kind set its level and pace, and the rate laws then rank candidate recipes, of which the top two or three are tested in the laboratory. On the synthetic data this workflow found a recipe within 5 points of the best of 12 for most feedstocks; on real feedstocks it remains to be shown. For scale-up, the ranked recipes can be passed to a transport model such as Lixa (Asgari, 2026), because the same chemistry gives different recovery in a column (Sect. 3.9).

4.7 Limits

The main benchmark is synthetic, and its generator shares most of the learner's structure. It favours LixaLearn by construction. Two of the three real datasets shaped the model and are not independent tests; the one held-out test was run once with its protocol fixed in advance, and it did not meet its criterion. The phosphogypsum and clay data come from the same laboratory group, and a held-out test on phosphogypsum from another laboratory would be the most direct check of the solubility-limited host. All real runs are single points at one time; the red mud bulk chemistry is taken from typical ranges, SiO_2 was imputed for the phosphogypsum and the clay, and the clay radius is an estimate from a sieve analysis. The model has no solution chemistry beyond Eqs. (5), (6) and (12). It ignores rare earth sulfate and phosphate precipitation, complexation by organic acids, exchange equilibrium with dissolved rare earths, alkalinity from sodium aluminosilicates and the selectivity between individual rare earths, and it predicts total rare earths only. The error band is nearly constant and calibrated on the synthetic feedstocks; on the real feedstocks it was too narrow. The recipe test uses one fold of 35 feedstocks. The pore-scale model is two-dimensional, uses synthetic packings and a single release rate, and shows the direction and size of transport effects, not a column design.

5 Conclusions

On 175 synthetic feedstocks of seven types, a model with leaching rate laws predicted unseen recipes better than tuned gradient boosting and a network of the same size without rate laws once test runs were available; after three test runs the errors were 5.4, 6.7 and 5.7 points. On real data the method was developed in the open, with each failure reported. A first held-out test on phosphogypsum failed and showed that the rate laws lacked a solubility limit. With a solubility-limited host and the common-ion effect of sulfate, three test runs predicted the other phosphogypsum runs to 7.4 points, against 10.9 for gradient boosting and 11.5 for the direct network; this is a development result. In the final held-out test, on an ion-adsorption clay, LixaLearn beat gradient boosting (3.3 against 5.5 points after three test runs) and the direct network (12.3), but not the mean of the test runs (2.7), so the criterion set in advance was not met. Physics-constrained learning transfers to real feedstocks when its rate laws have the right structure, and it does not when they do not. The next steps are a check of the rate laws against a few complete runs of each new kind of feedstock, and a held-out test on phosphogypsum from another laboratory.

Code and data availability

The LixaLearn v0.3.0 source code, the synthetic benchmark, the scripts that produce every number and figure in this paper, and the worked example of Appendix A are available from the author on request by email (shahram.asgari@uga.edu). The red mud data are from Ray et al. (2025), Table 4. The phosphogypsum data are from the supporting information of Li et al. (2022), Tables S5 to S7 (CC BY-NC 4.0), with the contact time and particle size from Li (2024) (CC BY 4.0). The clay data are from Anawati (2022), Table 6.1 and Appendix Table 14.1. The two test protocols and the version history are part of the code and data available on request.

Competing interests

The author declares no competing interests.

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Appendix A: One feedstock, step by step

This appendix follows one unseen synthetic feedstock through LixaLearn: a low-calcium coal fly ash from the first fold, with 4.2 % CaO, 56.1 % SiO₂, 28.7 % Al₂O₃, 9.2 % Fe₂O₃ and 406 ppm total rare earths. It was chosen in advance as the first low-calcium ash of the fold, not for its result. The script that produces it is part of the code available on request.

Step 1. Train.

The five networks are trained on the 140 feedstocks of the other four folds (840 runs). The training misfit is $\Delta = 6.9$ points.

Step 2. Guess.

From the chemistry alone, the networks place 12 % of the metal on exchange sites, 51 % in fast-dissolving minerals, 5 % in slow-dissolving minerals and 31 % in the locked fraction. The true shares are 3, 17, 45 and 34 %: the guess puts most of the releasable metal in fast-dissolving minerals, while the truth puts most of it in slow-dissolving glass (Sect. 3.3).

Step 3. Test.

Three bottle tests are run (Table A1), each sampled at seven times from 0.25 to 24 h.

Table A1. The three test runs on the example feedstock.

Test run	Reagent	C (mol L ⁻¹)	T (°C)	r (mm)	L/S (L kg ⁻¹)	Measured at 24 h (%)
1	sulfuric acid	0.23	60	0.002	10	64
2	sulfuric acid	0.07	80	0.016	10	62
3	citric acid	0.35	80	0.001	5	64

Step 4. Update.

The update (Eq. 14) fits the three test runs with mean errors of 1.7, 2.8 and 3.8 points (Fig. A1a). All parameters move little, because the penalty keeps the update close to the guess. The shares become 14, 54, 7 and 26 % (Fig. A1b), and the fitted reaction order is 0.67, against 0.8 in the generator. On the three runs the model was not shown, the error averaged over all seven sampling times was 5.2 points with no test runs and 2.8 points after three; at 24 h alone it was 5.8 and 2.5 points (Table A2). For this feedstock the test runs improved the prediction. The benchmark median after three test runs is 4.0 points, and one feedstock in ten has an error above 8.7 points.

Table A2. Prediction of the three unseen runs at 24 h, with 95 % bands.

Unseen run	Reagent	C (mol L ⁻¹)	T (°C)	Measured at 24 h (%)	k = 0 (%)	k = 3 (%)
1	citric acid	0.37	40	28	20 ± 14	27 ± 13
2	nitric acid	1.80	25	66	65 ± 14	71 ± 14
3	hydrochloric acid	0.84	90	69	61 ± 14	67 ± 14

Step 5. Rank.

The 12 candidate recipes of Sect. 3.5 are ranked by predicted recovery at 8 h (Fig. A1c). The top recipe is sulfuric acid at 1.03 mol L⁻¹ and 25 °C, predicted at 66 ± 14 %, with a true recovery of 64 %. The true best is hydrochloric acid at 0.34 mol L⁻¹ and 80 °C, with 65 %. The top two predictions differ by 1.5 points, well inside the band, so the ranking among the leading recipes is uncertain. In practice the top two or three recipes would be run and added to the update.

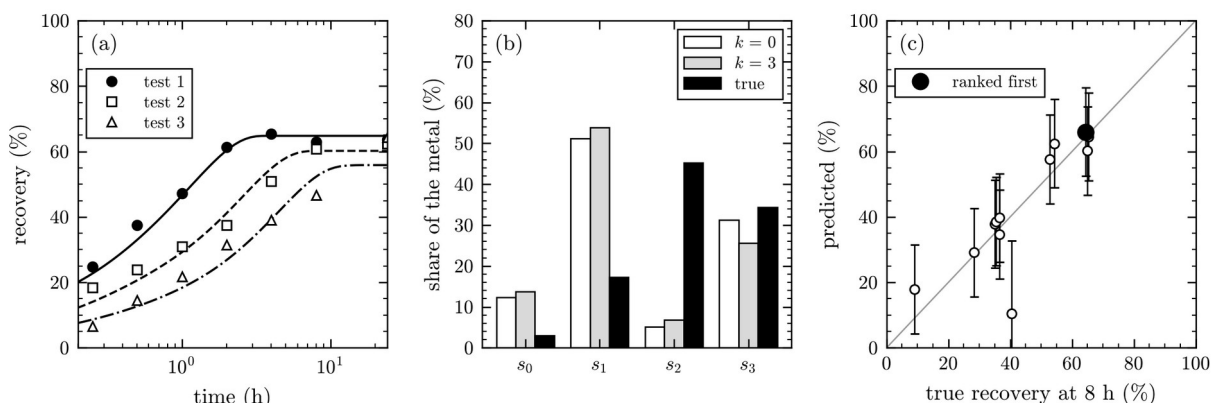


Figure A1. The worked example. (a) The three test runs (markers) and the fitted curves (solid, dashed and dash-dotted for test runs 1, 2 and 3); time on a logarithmic axis. (b) Host shares from the chemistry alone ($k = 0$), after three test runs ($k = 3$), and the truth. (c) Predicted against true recovery at 8 h for the 12 candidate recipes, with 95 % bands; the filled circle is the recipe ranked first, and the grey line is 1:1.

Appendix B: Settings of the synthetic data

Table B1 gives the composition ranges of the synthetic feedstocks, from which the bulk chemistry of each was drawn uniformly. The grade (ppm) was drawn log-uniformly within a range per type. Recipes were drawn as follows. The reagent was drawn from the allowed set of the type; the liquid-to-solid ratio from 2, 5, 10, 20 and 50 L kg⁻¹; the temperature from 10, 25, 40, 60, 80 and 90 °C (clays: 10, 25 or 40 °C, with 25 °C twice as likely); the particle radius log-uniformly between 0.001 and 0.05 mm for fly ash, sludge, red mud and phosphogypsum and between 0.1 and 2 mm otherwise. The concentration was drawn log-uniformly up to 2.5 mol L⁻¹ for acids and 1 mol L⁻¹ for salts, with a lower bound of 1.3 times the carbonate demand for 85 % of acid recipes and 0.05 mol L⁻¹ otherwise. In the reference model, citric acid has a capacity of three protons per mole and a driving activity equal to its free proton concentration (Eq. 6), and

every feedstock has a critical radius drawn log-uniformly between 0.01 and 0.03 mm. A share ϕ of the fast host is held in gypsum or anhydrite: ϕ is drawn between 0.7 and 0.95 for phosphogypsum (with m equal to its CaO content in mol kg^{-1}), between 0 and 0.3 for mine-water sludge and between 0 and 0.25 for high-calcium fly ash, and is zero otherwise; the gypsum solubility product is $2.4 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2}$ with a log-normal scatter of 20 %. The hidden rules from chemistry to host shares and rates are given in the code (synthetic.py).

Table B1. Ranges of the bulk chemistry in the synthetic data (minimum and maximum over the 25 feedstocks of each type). The red mud of Ray et al. (2025) was assigned 1.5 % CaO, 5 % SiO₂, 18.5 % Al₂O₃ and 51 % Fe₂O₃; the phosphogypsum of Li et al. (2022) has 35.4 % CaO, 0.11 % Al₂O₃ and 0.09 % Fe₂O₃, and the clay of Anawati (2022) 0.07 % CaO, 15.1 % Al₂O₃ and 21.0 % Fe₂O₃.

Type	CaO (wt %)	SiO ₂ (wt %)	Al ₂ O ₃ (wt %)	Fe ₂ O ₃ (wt %)
Weathered clay	0.1 to 1.0	45.8 to 59.3	26.1 to 37.9	2.3 to 7.7
Fly ash, low Ca	1.1 to 7.6	45.7 to 59.9	20.1 to 29.0	5.1 to 14.7
Fly ash, high Ca	18.8 to 29.5	30.4 to 39.6	15.3 to 20.0	4.1 to 7.0
Coal refuse	0.6 to 2.7	50.5 to 62.9	15.0 to 24.8	3.2 to 9.3
Mine-water sludge	5.8 to 22.6	2.1 to 9.9	5.8 to 19.1	31.3 to 57.3
Red mud	1.1 to 9.9	4.3 to 14.9	15.0 to 24.4	35.7 to 53.5
Phosphogypsum	28.1 to 37.9	1.1 to 9.8	0.1 to 1.0	0.1 to 0.5