Underestimation of alkaline dosage and precipitate amount during water treatment: Role of inorganic carbon and use of PHREEQ-N-AMDTreat

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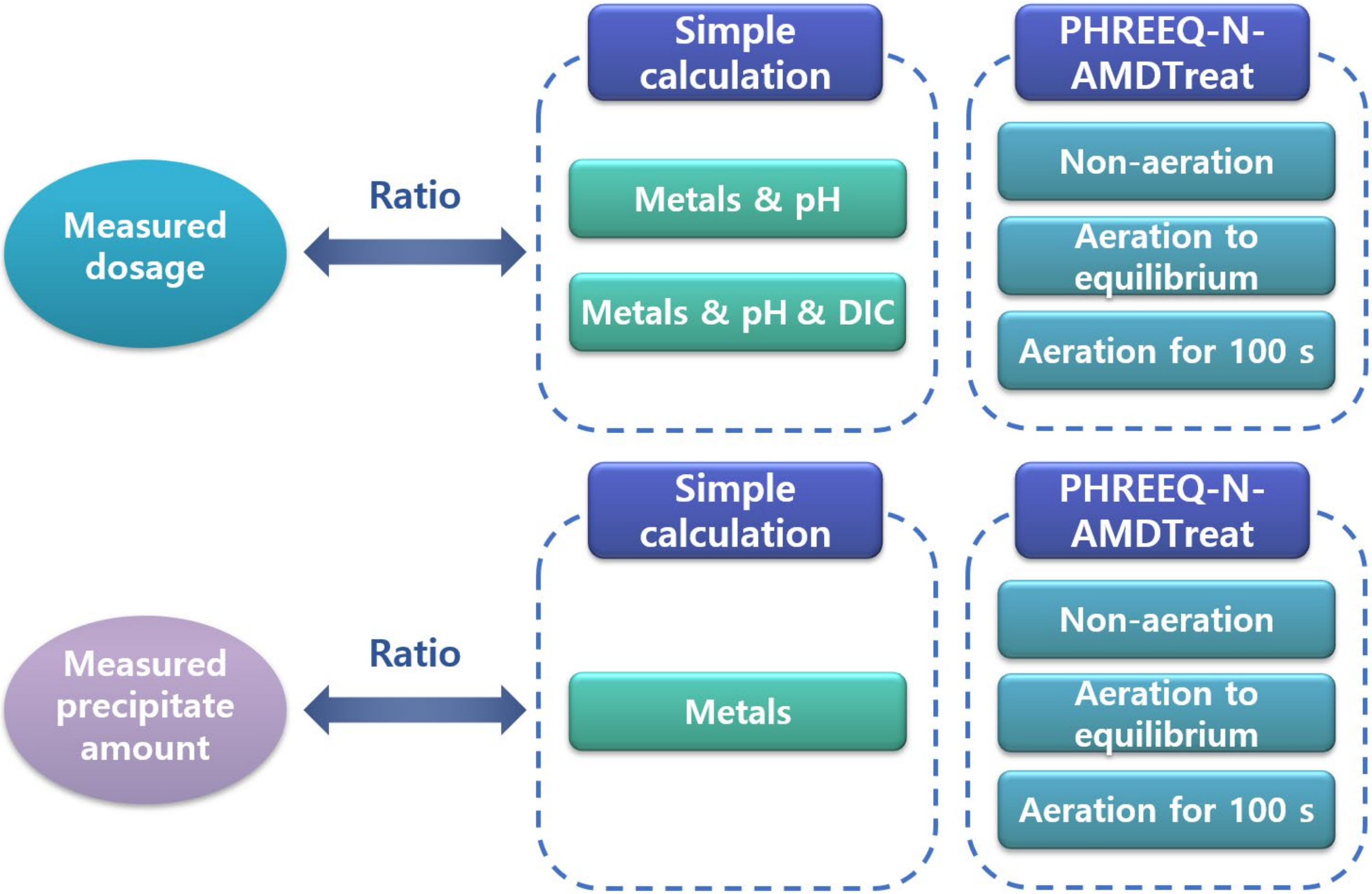
Introduction

- ✓ Alkaline agents are generally injected to treat mine drainage in active treatment
- ✓ Importance of **predicting the dosage of alkaline agents and amount of sludge**
  - ➢ Essential factor for the design and operation of those treatment facilities
  - ➢ Contribution to reduction of alkaline dosage & CO_2 generation during lime production
- ✓ Alkaline dosage and sludge amount are **often calculated based on concentrations & pH**
  - ➢ Net acidity is applied for alkaline dosage calculations
  - ➢ Can lead to **inaccurate results**
- ✓ To remove Mn, **pH** typically needs to be increased to **>8.3**
  - ➢ Necessary dosage of alkaline agents **exceeds the net acidity**

Introduction

- ✓ At pH >8.3, **HCO_3^- becomes the principal component of acidity** (Morel and Hering, 1993; Stumm and Morgan, 1996; Langmuir, 1997)
  - Acidity = $2[H_2CO_3^0] + [HCO_3^-] + [H^+] - [OH^-]$ (pH: 8.3 to 11.0)
  - Increase in alkaline dosage is attributed to dissolved inorganic carbon (DIC)
- ✓ **Precipitation of $CaCO_3$** also influences alkaline dosage and sludge amount (Nordstrom, 2020)
- ✓ **PHREEQ-N-AMDTreat** by USGS (Cravotta, 2020)
  - Utilized for assessing efficiency and design of mine drainage treatment facilities
  - **Caustic Titration module** considers DIC to predict alkaline dosage, precipitate amount, and concentrations with varying pH
- ✓ Factors affecting alkaline dosage and relevant prediction need to be studied (particularly at pH of >8.3)

Methods


Measured dosage
Ratio
Simple calculation
Metals & pH
Metals & pH & DIC
PHREEQ-N-AMDTreat
Non-aeration
Aeration to equilibrium
Aeration for 100 s
Measured precipitate amount
Ratio
Simple calculation
Metals
PHREEQ-N-AMDTreat
Non-aeration
Aeration to equilibrium
Aeration for 100 s

Methods

✓ **Alkaline dosage assessment through batch experiments with increasing pH**

1) **Influent from 7 active & semi-active treatment** facilities including Mn, with varying characteristics
    - 6 sites: hydrated lime, 1 site: caustic soda
2) **Artificial raw water**
    - Mixed Fe + Mn (28.5-31.3 mg L^{-1}), only Mn (5.7-21.2 mg L^{-1}), only Fe (32 mg L^{-1})
    - $NaHCO_3$ & $CaSO_4 \cdot 2H_2O$ were also added

✓ **Modeling methods**

✓ **PHREEQC v. 3.7**: Calculation of saturation indices (SIs) & prediction of concentrations with varying lime dosages

✓ **PHREEQ-N-AMDTreat**: Prediction of lime dosage & precipitate amount
- **Comparison among non-aeration, aeration to equilibrium, and pre-aeration conditions**

Experiments for dosages of alkaline agents

✓ Calculation of alkaline dosage based on metal concentrations and pH

- $D_m = -\Delta([H^+] + 3[Al] + 2[Cu] + 2[Fe^{II}] + 3[Fe^{III}] + 2[Mn] + 2[Zn]) \times \frac{74.095}{2}$

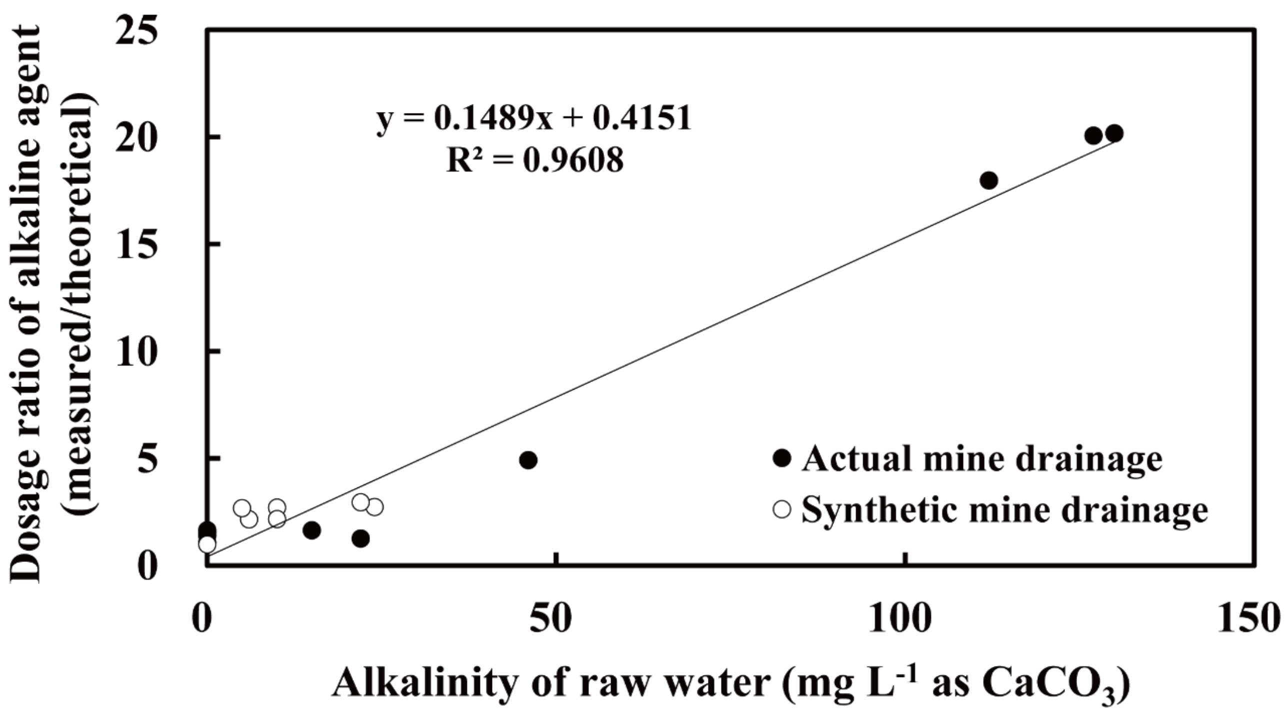
Facil-ity	Exp.	Sample	pH	Alk.	Al	Cu	Fe^{II}	Fe^{III}	Mn	Zn	Measured/Predicted alkaline dosage	
											Metals & pH	Metals, pH & DIC
			(-)	(mg L^{-1} as $CaCO_3$)	(mg L^{-1})						(-)	(-)
Ham-tae	1st	Raw water	6.93	112	n.d.	n.d.	0.70	0.71	2.70	0.031	-	-
		Treated	8.88	133	0.03	n.d.	n.d.	0.03	1.45	0.001	1799%	124%
Il-gwang	1st	Raw water	2.49	n.d.	32.9	17.2	4.90	182.7	7.23	15.3	-	-
		Treated	8.64	38	0.26	0.008	n.d.	0.03	1.63	0.048	108%	-
Ok-dong	1st	Raw water	6.99	15	n.d.	0.023	n.d.	0.05	19.22	51.6	-	-
		Treated	10.70	32	n.d.	n.d.	n.d.	0.01	0.03	0.129	166%	140%
Sam-bo	1st	Raw water	6.92	22	2.36	n.d.	2.45	2.45	48.96	45.6	-	-
		Treated	10.07	35	0.14	n.d.	0.02	0.02	0.21	0.056	127%	110%
	2nd	Raw water	6.98	22	2.75	0.004	n.d.	0.01	51.68	6.35	-	-
		Treated	9.94	28	0.12	n.d.	n.d.	n.d.	0.76	0.108	127%	115%

Experiments for dosages of alkaline agents

Facil-ity	Exp.	Sample	pH	Alk.	Al	Cu	Fe^{II}	Fe^{III}	Mn	Zn	Measured/Predicted alkaline dosage	
											Metals & pH	Metals, pH & DIC
			(-)	(mg L^{-1} as $CaCO_3$)	(mg L^{-1})						(-)	(-)
Uljin	1st	Raw water	2.62	n.d.	11.9	0.032	n.d.	**80.16**	**30.47**	1.463	-	-
		Treated	9.84	32	0.25	n.d.	n.d.	0.21	0.43	0.001	166%	-
	2nd	Raw water	2.60	n.d.	11.9	0.045	1.20	**85.93**	**30.39**	1.333	-	-
		Treated	9.85	31	0.18	n.d.	0.09	0.05	0.66	0.003	141%	-
	3rd	Raw water	2.65	n.d.	12.9	0.051	1.05	**77.45**	**33.81**	1.829	-	-
		Treated	9.92	21	0.07	n.d.	n.d.	0.01	0.53	0.058	154%	-
Yeon-Hwa	1st	Raw water	7.91	130	0.02	n.d.	0.03	0.03	4.44	0.090	-	-
		Treated	8.99	55	0.02	n.d.	0.01	0.01	1.66	0.003	**2018%**	113%
	2nd	Raw water	8.69	127	n.d.	n.d.	n.d.	n.d.	4.63	0.162	-	-
		Treated	8.86	47	n.d.	n.d.	n.d.	n.d.	1.76	0.063	**2008%**	142%
2nd Yeonhwa	1st	Raw water	8.27	46	0.04	n.d.	0.02	0.01	**10.61**	0.105	-	-
		Treated	9.83	34	0.04	n.d.	n.d.	0.18	0.86	n.d.	**493%**	166%

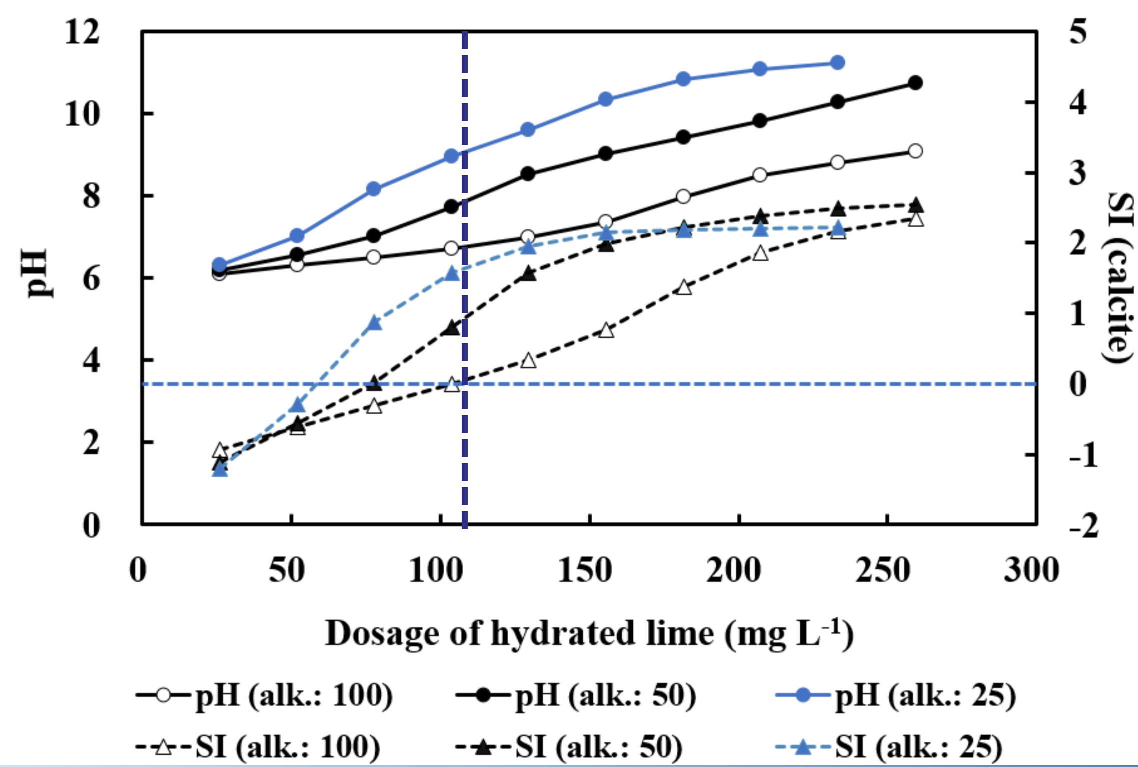
Experiments for dosages of alkaline agents

- ✓ Dosage ratio of alkaline agent (measure/theoretical) exhibited a positive relationship with the alkalinity of the raw water
- ✓ **Alkalinity predominantly influenced dosage of alkaline agent at pH of >8.6**
  - $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$



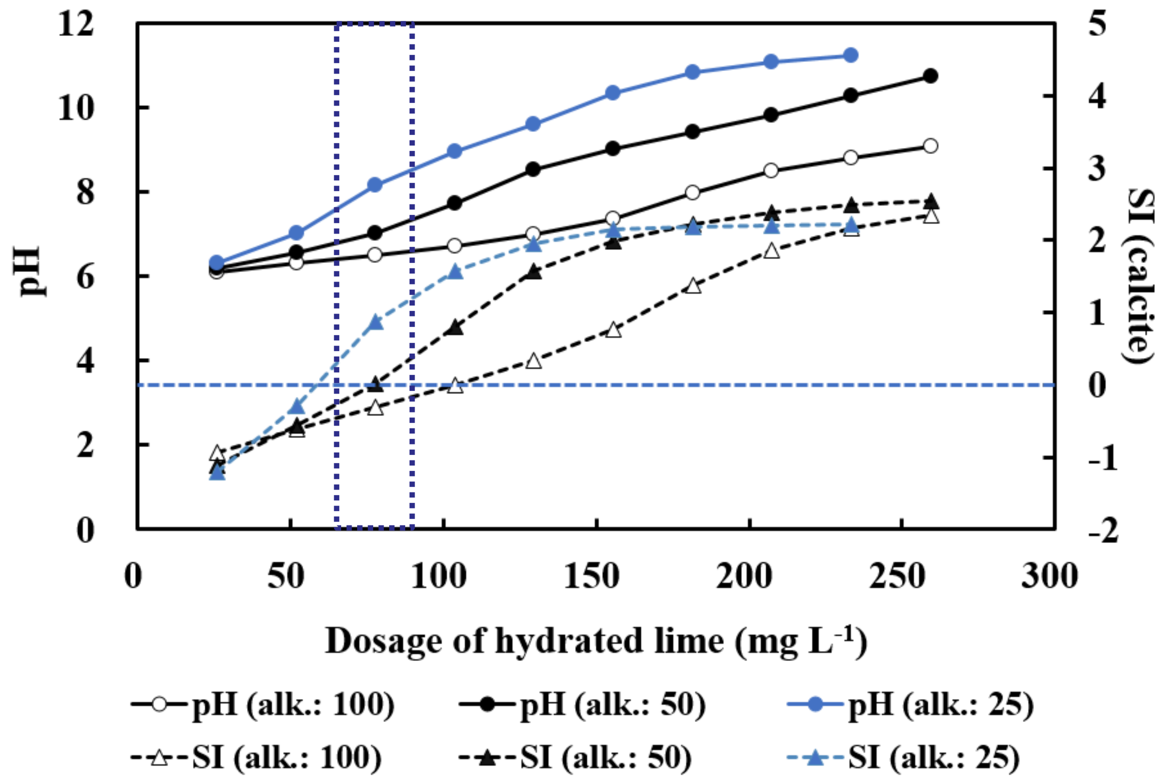
Geochemical modeling to differentiate the effects of DIC and precipitation

- ✓ PHREEQC modeling **to discern effects of DIC & precipitation** on lime addition
- ✓ More hydrated lime was required to achieve the same pH with increasing alkalinity of the raw water
- ✓ At identical dosages, SIs of calcite were generally higher in cases of lower alk.
  - In raw water with lower alk., pH more easily increased to increase CO_3^{2-}



Geochemical modeling to differentiate the effects of DIC and precipitation

- ✓ **Even if not all samples were saturated with calcite, pH variation by alk. was high**
- ➢ **Alk., rather than calcite precipitation, is the primary factor to increase lime dosage**
  - Additionally, brucite($Mg(OH)_2$) & gypsum($CaSO_4 \cdot 2H_2O$) precipitation influence

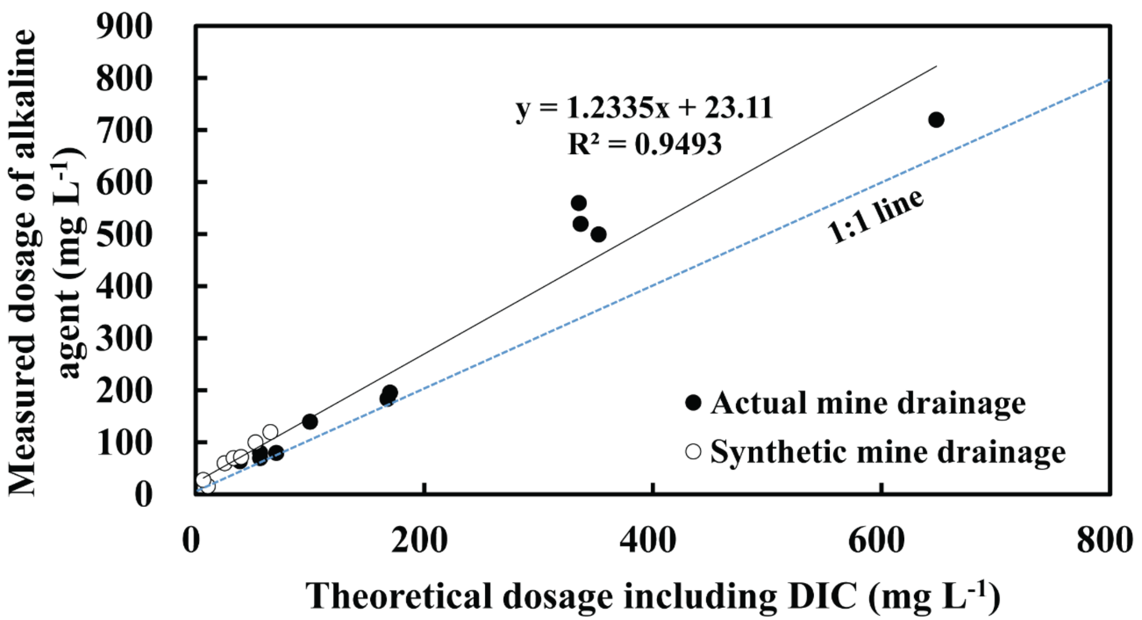


Effect of DIC in calculating alkaline agent dosage

✓ Calculation of alkaline dosage considering metal concentrations, pH **and DIC**

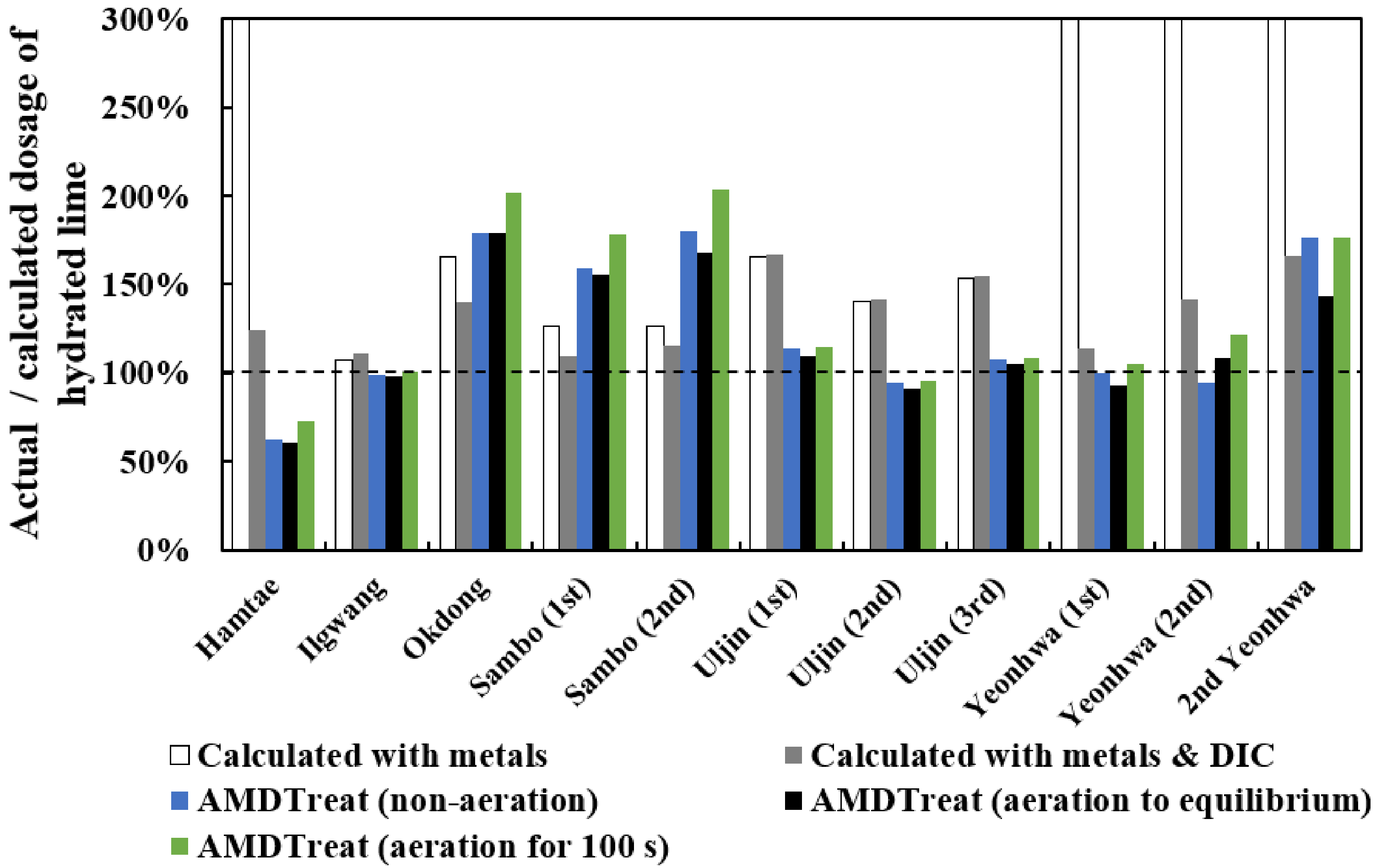
- $D_d = -\Delta([\mathrm{H}^+] + 3[\mathrm{Al}] + 2[\mathrm{Cu}] + 2[\mathrm{Fe}^{II}] + 3[\mathrm{Fe}^{III}] + 2[\mathrm{Mn}] + 2[\mathrm{Zn}] + \mathbf{2[H_2CO_3^0] + [HCO_3^-]}) \times \frac{74.095}{2}$

- Predicted dosages considering DIC change were **similar to measured values**
  - But measured values were higher (123%) possibly due to calcite precipitation
  - **Change in DIC is difficult to be simply calculated**



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

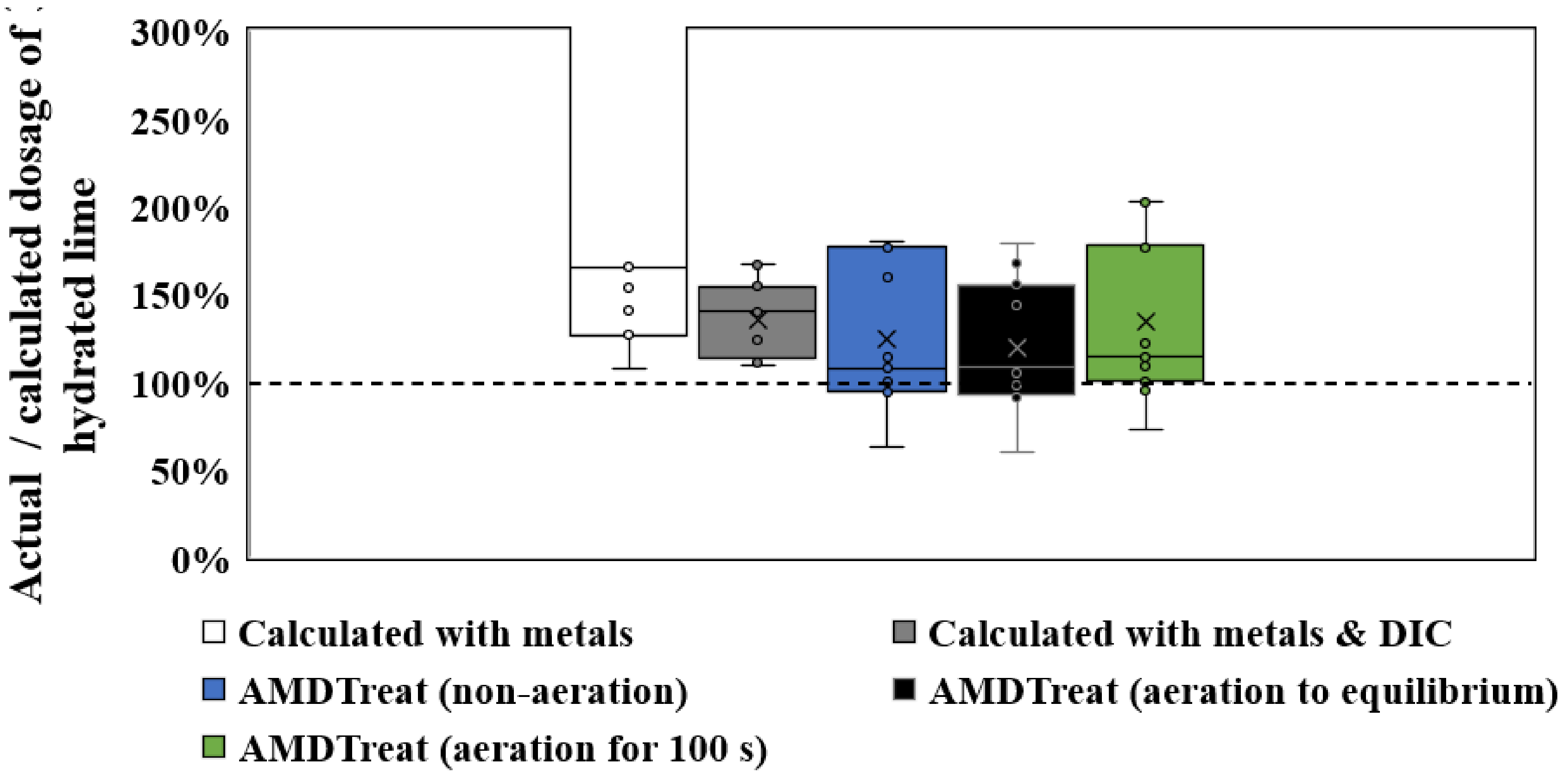
- ✓ Comparation of predicted & measured dosages among 3 aeration conditions of PHREEQ-N-AMDTreat



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

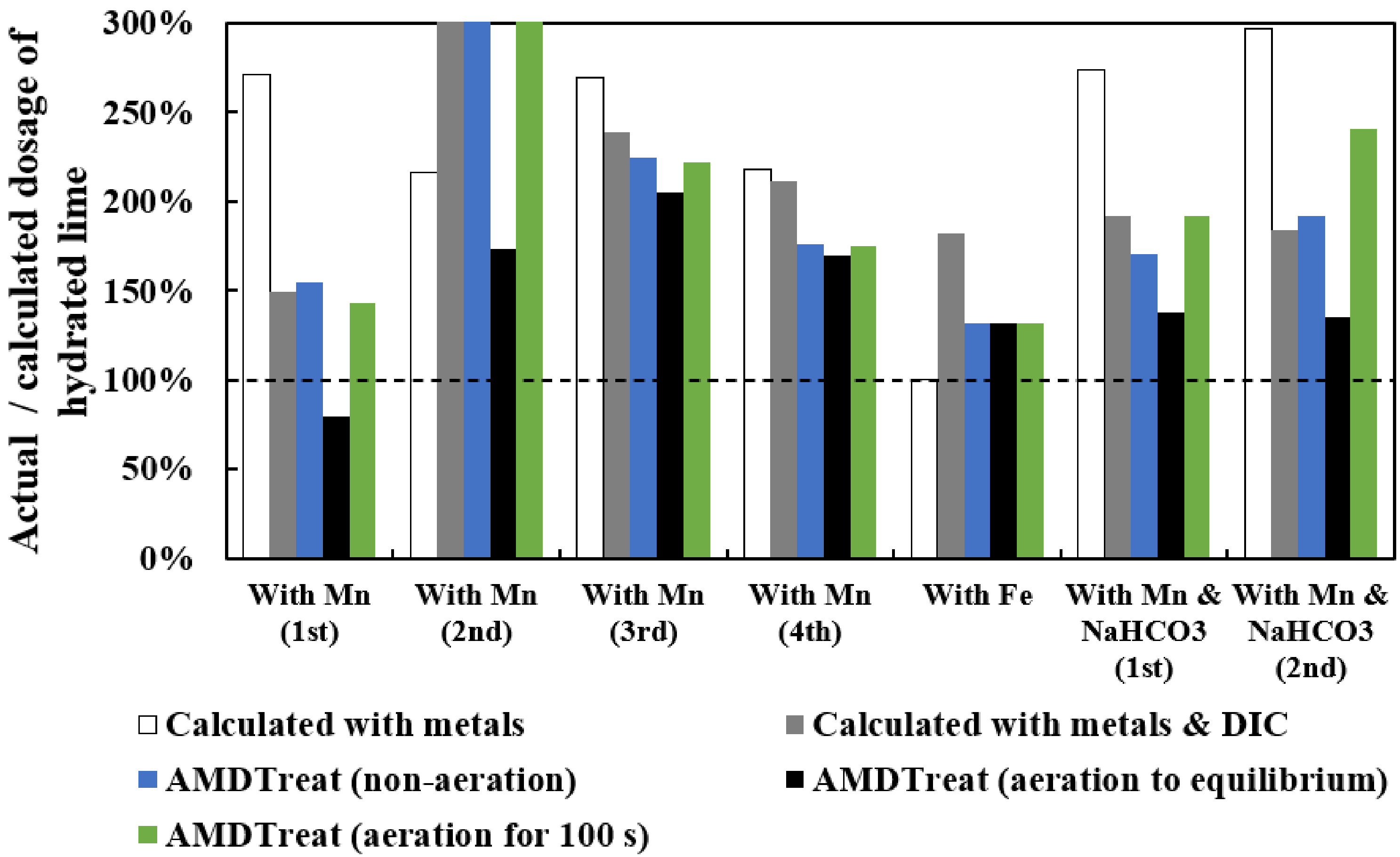
✓ Aeration condition closest to achieving 100% accuracy: **Aeration to equilibrium**

- **119% in average**



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

✓ Comparation of predicted & measured dosages among 3 aeration conditions of PHREEQ-N-AMDTreat – **artificial mine drainages**

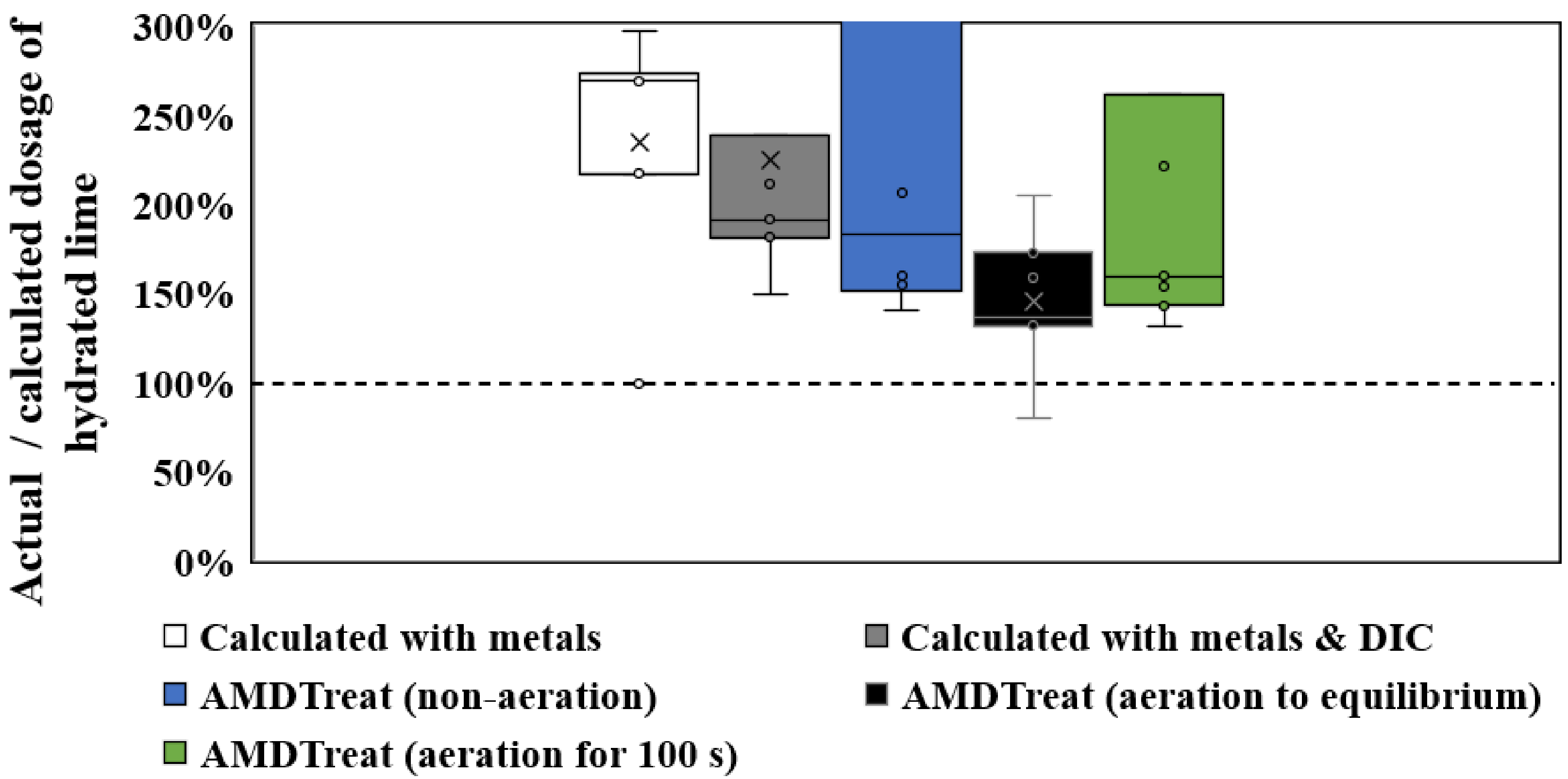


Assessment of geochemical model prediction of alkaline dosage and precipitate amount

✓ Aeration condition closest to achieving 100% accuracy: **Aeration to equilibrium**

- **147% in average**

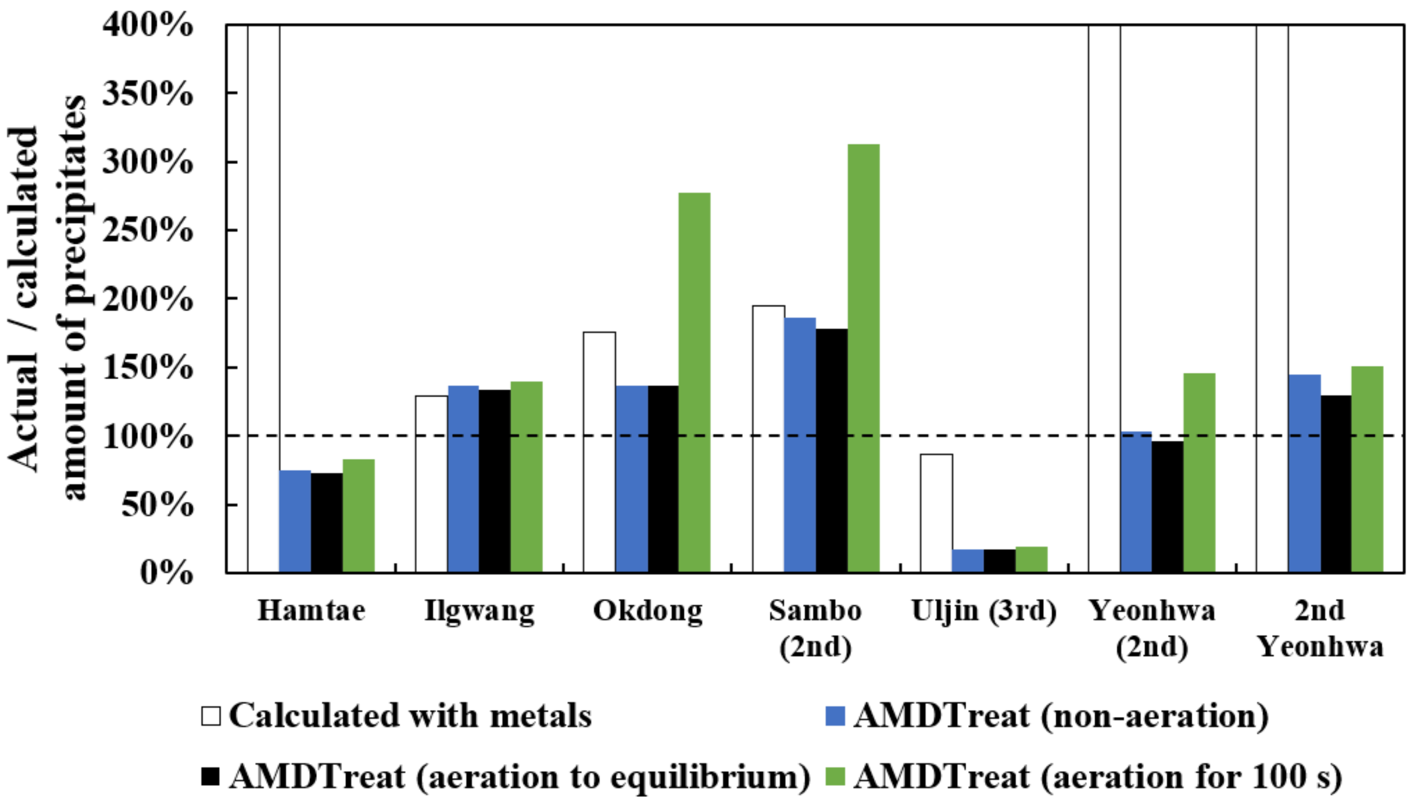
1) While Mn actually decreased, **the other conditions predicted that Mn would remain**
2) **The other conditions overestimated alkalinity to underestimate lime dosage**



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

✓ Comparation of predicted & measured dosages among 3 aeration conditions of PHREEQ-N-AMDTreat

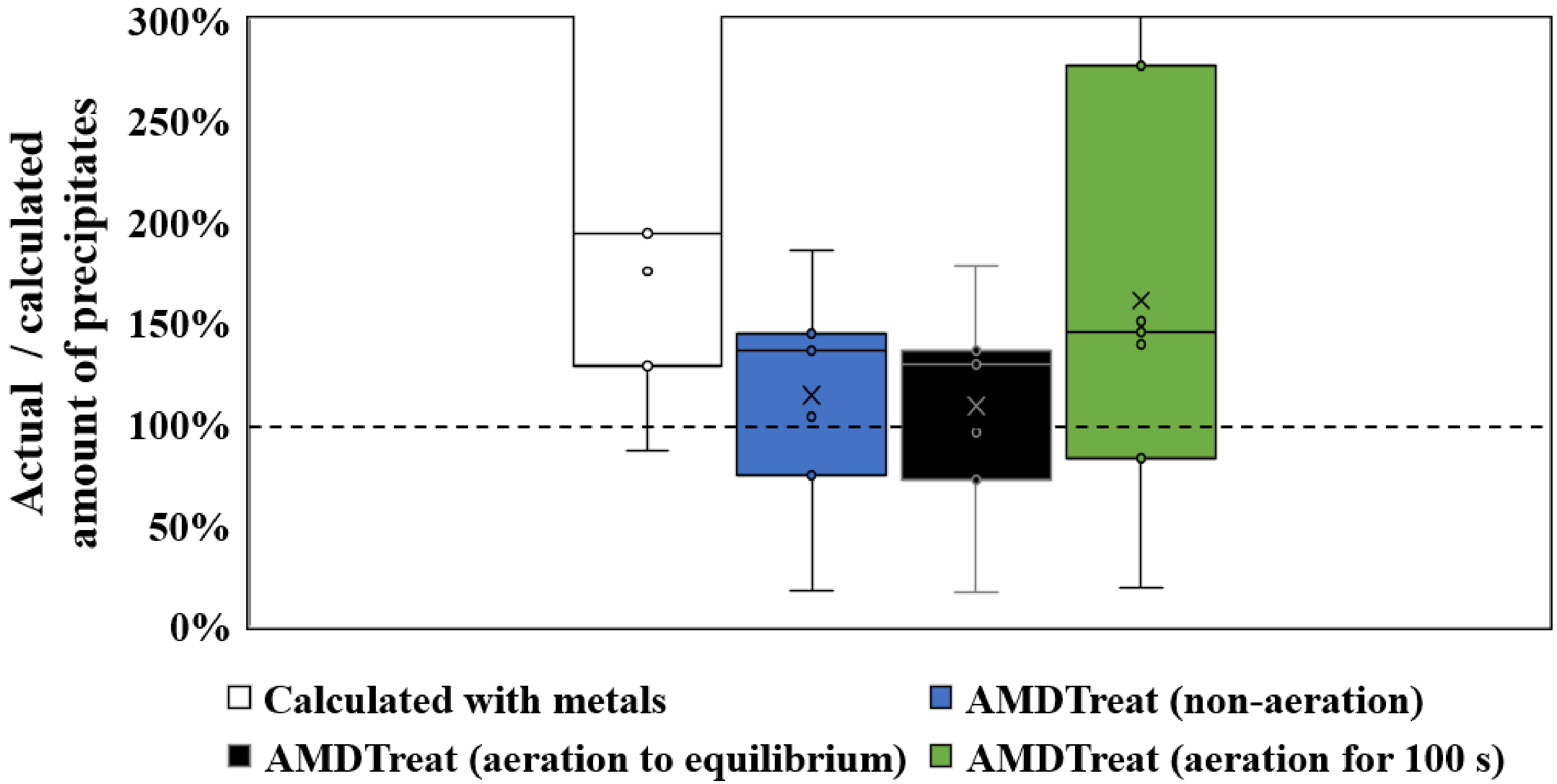
- Precipitate amounts for actual mine drainages / **Simple calculation: 86-5155%**



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

✓ Aeration condition closest to achieving 100% accuracy: **Aeration to equilibrium**

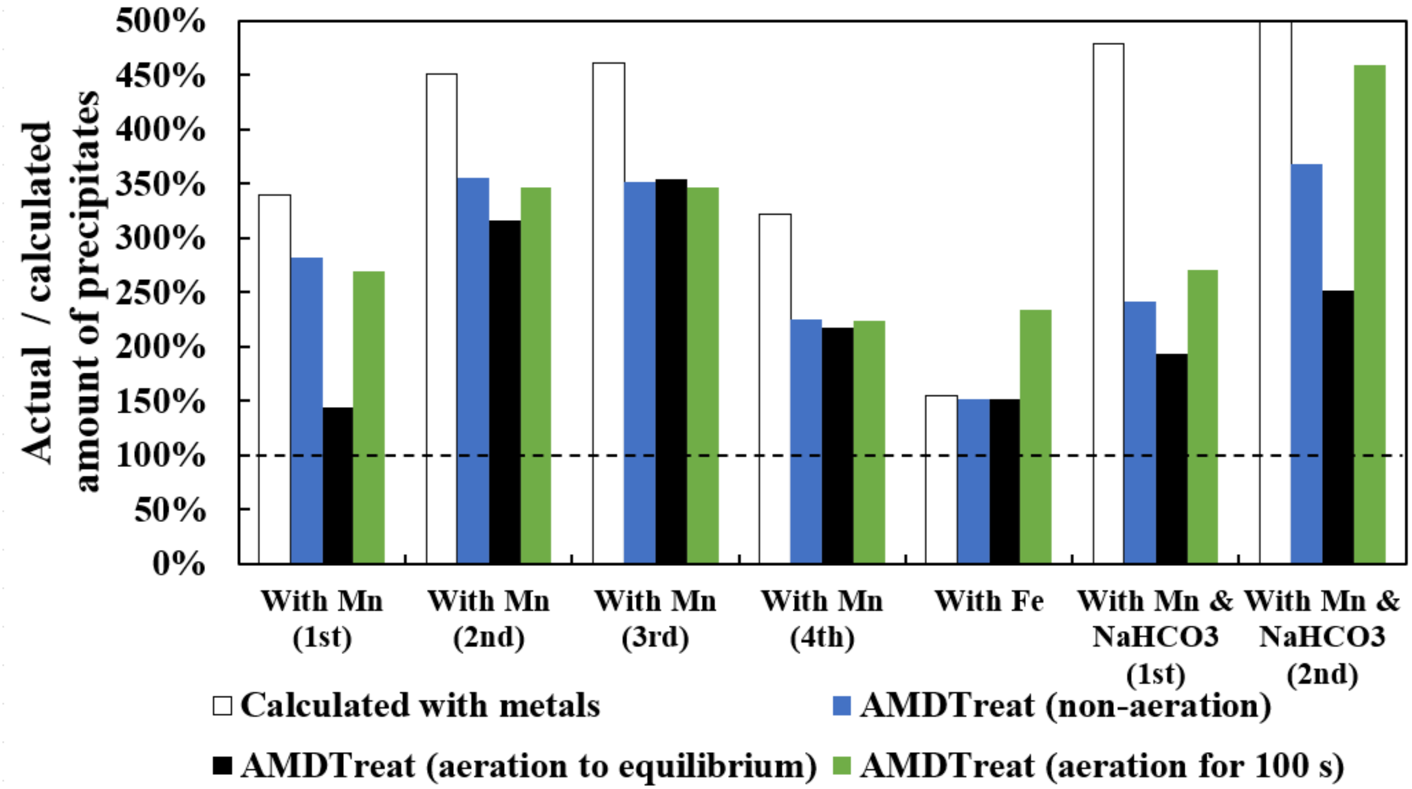
- **124% in average**



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

✓ Comparation of predicted & measured dosages among 3 aeration conditions of PHREEQ-N-AMDTreat – **artificial mine drainages**

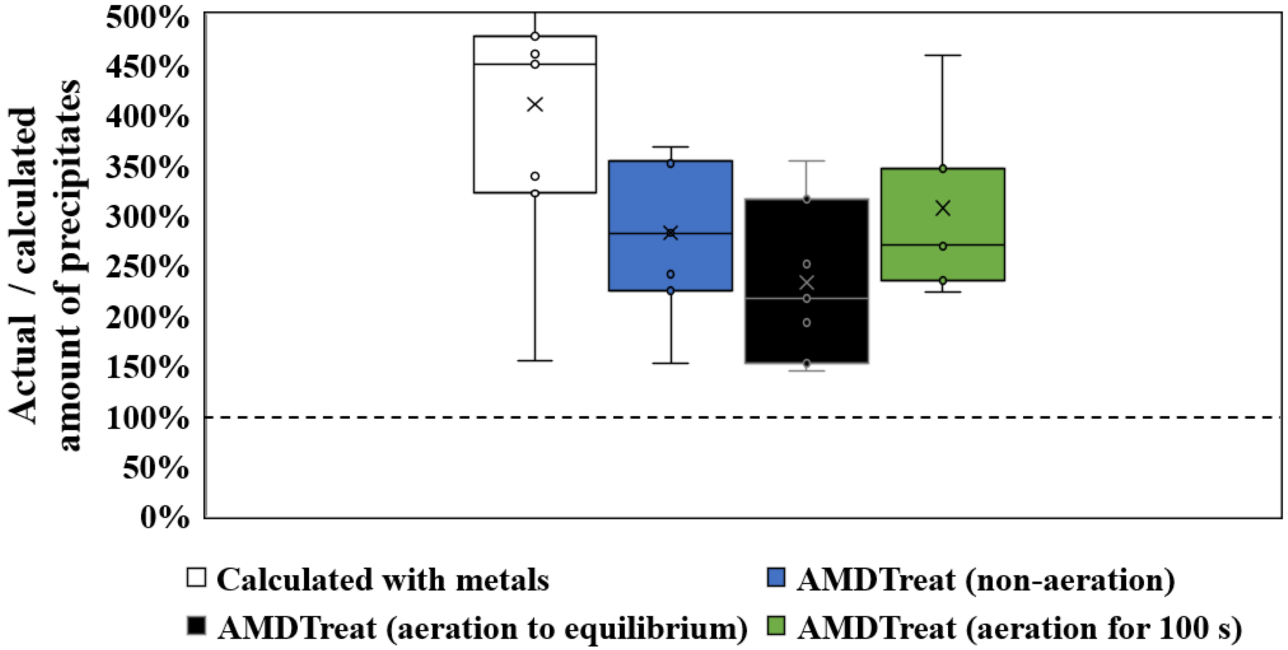
- **Simple calculation: 86-5155%**



Assessment of geochemical model prediction of alkaline dosage and precipitate amount

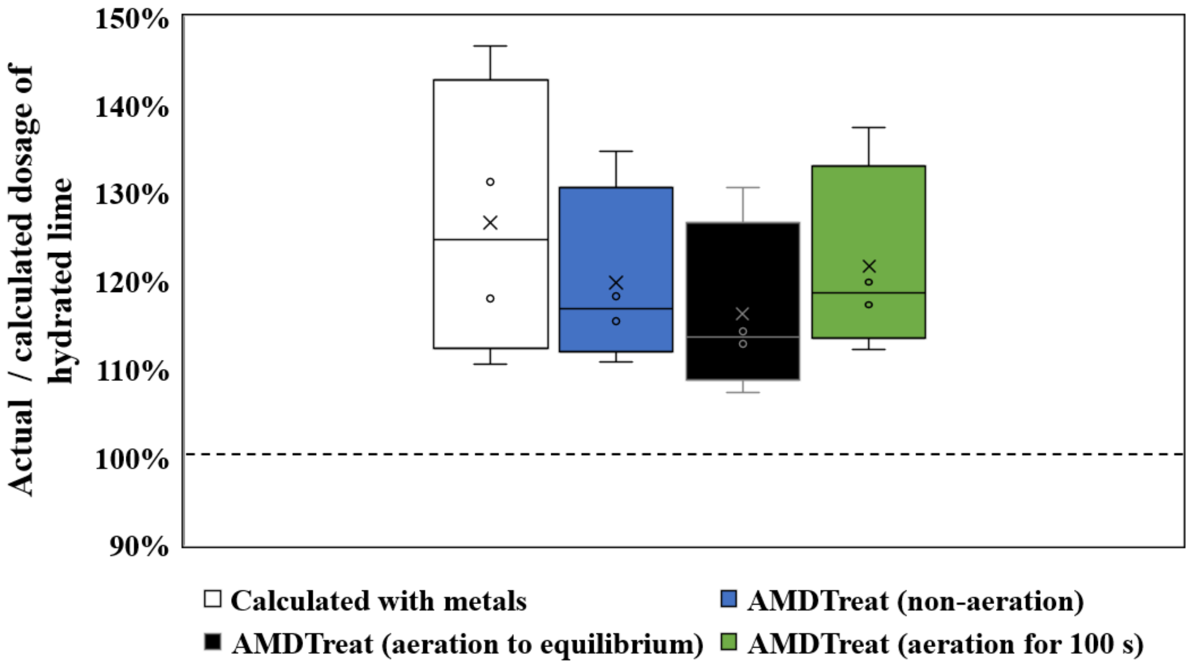
✓ Aeration condition closest to achieving 100% accuracy: **Aeration to equilibrium**

- **233% in average**
- Related to aforementioned reasons → Most accurate simulation of effects including calcite precipitation by DIC



Verification example in full- and pilot-scale treatment facilities

- ✓ Verification of lime dosage using operational data of Samtan treatment facilities
- ✓ Aeration condition closest to achieving 100% accuracy: **Aeration to equilibrium**
  - **116% in average**



- ✓ Verification of precipitate amount using pilot-scale experiments at Samtan mine
- ✓ Condition closest to achieving 100% accuracy: **Aeration to equilibrium (97%)**

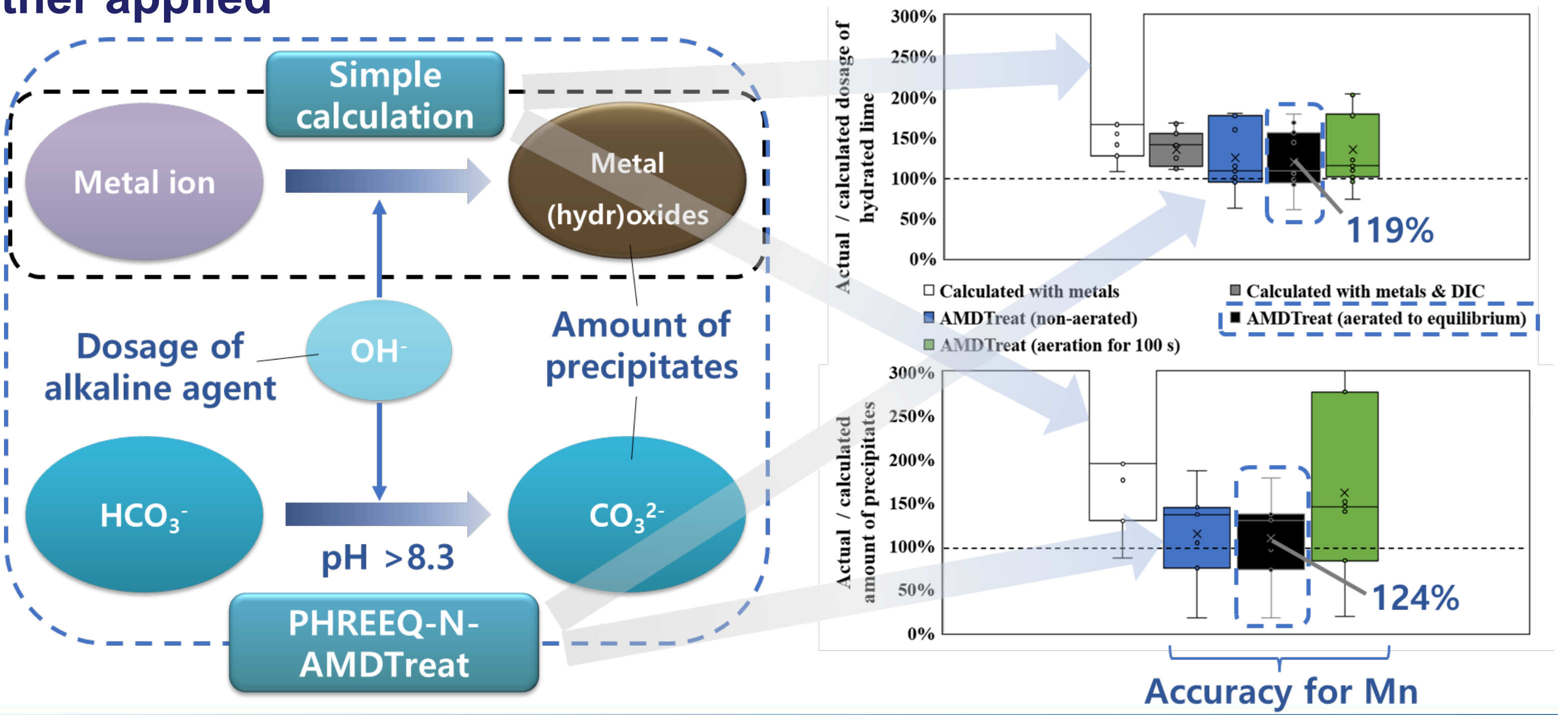
Conclusions

✓ **Principal cause of underestimation of lime dosage is DIC in influent**

- Other causes include precipitation of calcite & brucite

✓ **Aeration to equilibrium condition of PHREEQ-N-AMDTreat** was the most suitable for predicting lime dosage and precipitate amount (particularly if pH >8.3)

✓ **After modeling, 119% (lime dosage) & 124% (precipitate amount) can be further applied**



Thank you for your attention

** Further questions & discussion: kdukmin8@sangji.ac.kr*

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