Geochemical interpretation of sequential extraction results from the Ajka Bauxite-Residue

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- Presentation of the applied method
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Sequential extraction methods in general

- Nowadays, it is one of the most commonly used geochemical analysis near the pH dependent test, although it is more expensive.
- Sequential extraction method was established several decades ago in order to evaluate trace element availability (originally) in soil.
- By time it proved the applicability in case of rocks as well.
- It is a perfect geochemical tool to detect which is that mineral phase or group where the searched element is bounded.
- From the first one, more generations of the test are invented.

Sequential extraction methods

- ***Tessier type 5 steps (1979)***
  - Exchangeable fraction
  - Bound to carbonates
  - Bound to Fe-Mn oxides
  - Bound to organics matter
  - Residual
- ***BCR type 3 steps (1993) /by Standards, Measurement and Testing Programme; formerly BCR/***
  - Exchangeable fraction
  - Metals bound to Fe-Mn oxides
  - Metals bound to organics matter and sulphides
  - Residual

Sequential extraction methods

- ***Dold type 7 steps (2001)***
  - Water soluble fraction
  - Exchangeable fraction
  - Fe^{III} oxyhydroxides
  - Fe^{III} oxides
  - Organics and secondary (Cu) sulphides
  - Primary sulphides
  - Residual

Sequential extraction methods

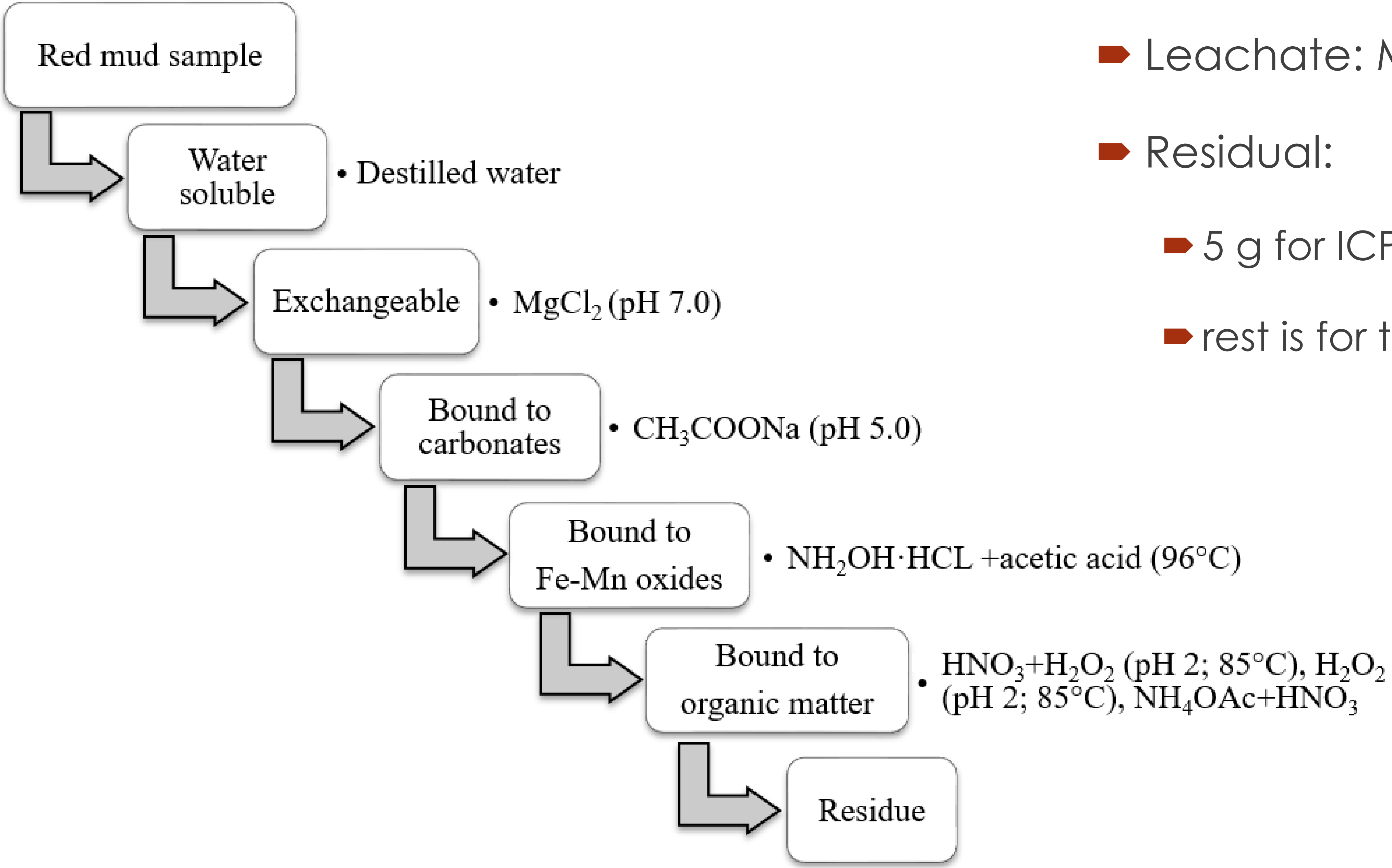
- ***Tessier type (1979) method modified by Gu et al. (2018)***
  - Water soluble fraction
  - Exchangeable fraction
  - Bound to carbonates
  - Bound to Fe-Mn oxides
  - Bound to organics
  - Residual

Gu, H., Wang, N., Hargreaves, J. S. J. (2018): **Sequential extraction of valuable trace elements from Bayer process-derived waste red mud samples.** Journal of Sustainable Metallurgy, Vol. 4, pp. 147-154.

Our choice: Gu et al. (2018) method

- **But why?**
- It is specified for red mud (pH 13-14), as the residual of the Bayer process.
- It has good mineral phase separation because of:
  - the large number of the steps
  - the selectively choosen chemicals let better detection of the mineral groups
  - compare to „old" Tessier or BCR method, in them some steps leach out more than one mineral phase in the same step
  - Dold method has the same separation but it is invented for Cu minerals
- Key answers: 1, good separation of the phases; 2, specified for red mud

The applied Gu et al. (2018) method



- Leachate: MP-AES
- Residual:
  - 5 g for ICP-ES and ICP-MS
  - rest is for the next step

Method has already chosen, but which sample(s) will be analized from the 41 species?

- Cannot forget: 1 sample = 5-times leaching process (time consuming), 5 leachate and 5 residual material.
- Based on the chemical and mineralogical results, the cell VIII. was chosen in a vertical set of the top 5 spieces, which mean samples from depth of 1, 2, 3, 4 and 5 m.
- 20-times test size enlargement was applied, as intsead of 3 g, the starting amount was modified to 60 g of the sample.
- The same enlargement was used also for the amounts to the reagents.

Mineralogical composition of the chosen samples

- Based on these mineralogical results, the Gu et al. (2018) method can be a good choice.
- Theoretically there should have no overlapping of dissolution of the similar mineral group in the same step.

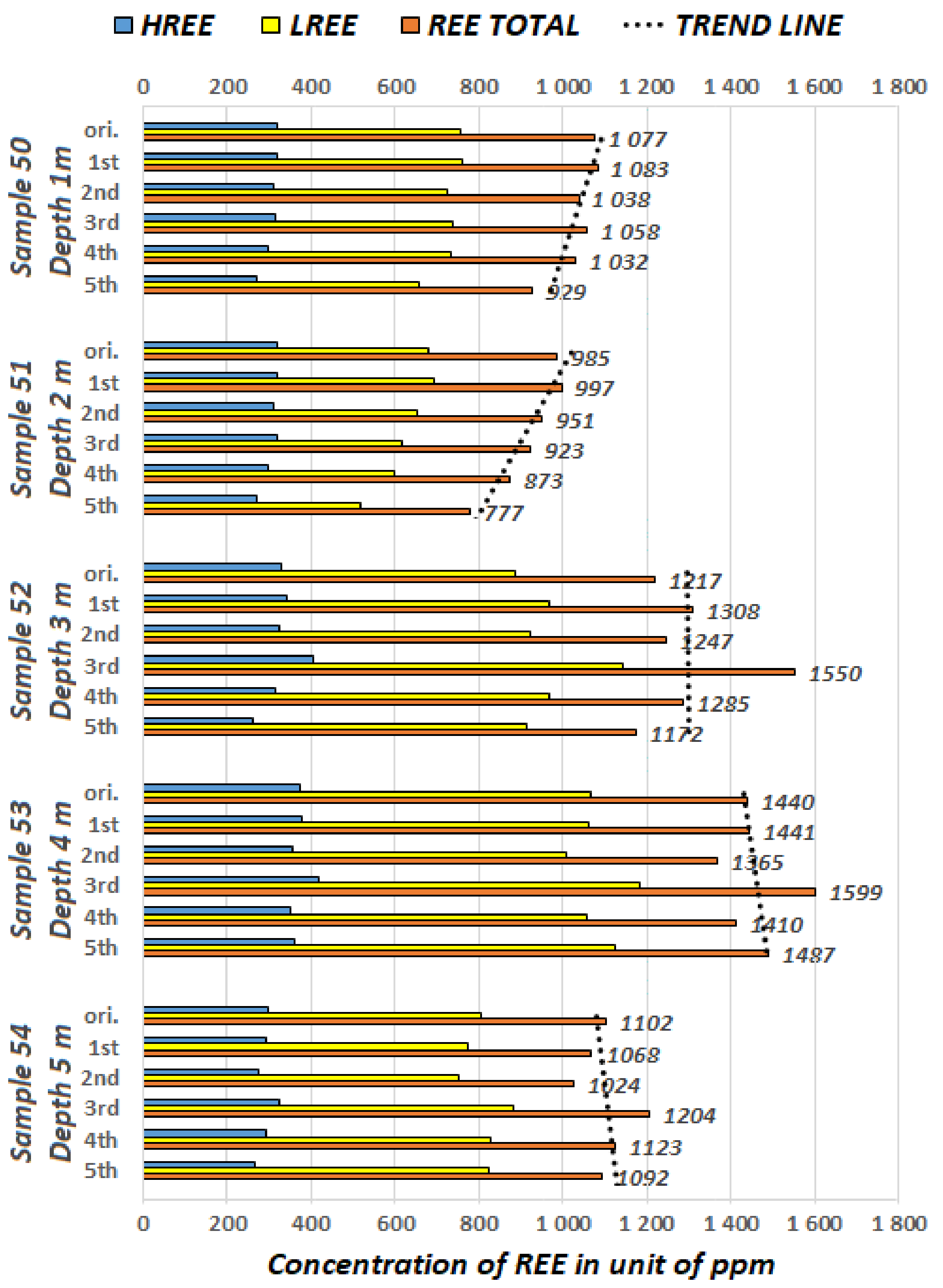
Sample *		50	51	52	53	54
Sampling depth (m)		1	2	3	4	5
Hematite	Fe_2O_3	35.2	34.8	34.9	35.6	37
Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$	17.1	9.1	19.9	22.2	18.4
Gibbsite	$Al(OH)_3$	5.1	3.0	1.7	2.2	1.2
Calcite	$CaCO_3$	6.6	12.0	7.5	10.3	9.6
Dolomite	$CaMg(CO_3)_2$	0.8	2.0	0.9	0.0	1.4
Katoite	$Ca_3Al_2(SiO_4)_{1.5}(OH)_6$	2.5	1.2	4.2	3.0	2.3
Goethite	FeOOH	16.6	19.3	12.0	3.7	7.2
Boehmite	AlOOH	1.4	2.7	1.4	0.7	2.3
Quartz	SiO_2	0.5	0.4	0.5	0.5	0.2
Kaolinite	$Al_2Si_2O_5(OH)_4$	1.9	0.8	0.6	2.2	0.7
Cancrinite (OH)		2.8	1.8	1.8	3.6	2.7
Amorphous		8.4	12.0	13.3	14.6	15.5
Others**		1.1	0.7	1.3	1.4	1.5

* The unit is given in m/m%.

** Total of hibschite, anatase, diaspore, manganosite and aragonite.

SE results from the residuals

- Three trend line can be read out:
- Upper zone (sample 50 and 51; 1 & 2 m)
  - Decreasing REEs content => dissolving
  - REEs bound mainly to carbonates and Fe phases
- Middle zone (sample 52; 3 m)
  - Stable REEs content => partly dissolving
  - The dissolving REEs keep balance with the enrichment effect in the residual.
- Lower zone (sample 53 and 54; 4 & 5 m)
  - Increasing REEs content => higher the enrichment effect than the dissolution rate
  - REEs bound mainly to REE phosphates or silicates



Conclusion

- After literature work, proper sequential extraction method was chosen.
- From the 41 species of the red mud samples, 5 were chosen after checking the chemical and mineralogical compositions of them.
- Near the difficulties of the samples, the test was prosperous.
- From the result of the sequential extraction and from the trend lines of the changes of the REEs three type of zones were established.
- At the top, the REEs dominantly bound to the carbonate and Fe phases, while in lower they are dominantly in the phosphate and silicate phases.

Thank you for your kind attention!