UNIVERSITY OF PRETORIA / UNIVERSITEIT VAN PRETORIA
DEPARTMENT OF PLANT PRODUCTION AND SOIL SCIENCE /
DEPARTEMENT PLANTPRODUKSIE EN GRONDKUNDE

GKD 320
SOIL CHEMISTRY / GRONDCHEMIE

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Semester test / *Semestertoets*
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Time / *Tyd*: 90 min
Marks / Punte : 40

Question 1 / Vraag 1

With an appropriate example, explain the Ostwald step rule for precipitation and the implication of that on the mineral stability in the soil./ *Met 'n gepaste voorbeeld, bespreek die Ostwald reël vir presipitasie en die implikasie daarvan vir mineraal stabiliteit in die grond*. (6)

1) The Ostwald step rule dictates that solid phases with larger surface are precipitate first; **(1 mark)**
2) The precipitate are typically fine crystalline minerals or amorphous phases which are more soluble than more crystalline phase; **(1 mark)**
3) The reason for this is that phase change (solute to solid) requires energy and an energy barrier that must be overcome first; **(1 mark)**
4) It is more energetically favourable for a solid that forms a large surface to precipitate first; **(1 mark)**
5) The fine crystalline minerals or amorphous phases are called metastable precursor phases; **(1 mark)**
6) They are not thermodynamically stable and will transform to more stable and crystalline phases with time **(1 mark)**
7) An example is the formation precipitation of ferrihydrite from the soil solution which transform with time to more crytalline lepidocrocite, goethite or hematite **(1 mark)**

Question 2 / Vraag 2

Briefly discuss the differences you expect between the mineralogy of the phyllosilicate minerals of a <u>highly weathered soil</u> and a soil collected in an <u>environment subjected to mild or intermendiate weathering</u>. / *Bespreek die mineralogiese verskille wat jy verwag tussen die fillosilikate van 'n <u>hoogs verweerde grond</u> en die van 'n grond wat versamel is in 'n omgewing onderworpe was aan matige of intermediere verwering.* (10)

<u>Highly weathered soil</u>
1) The phyllosilicate expected here is kaolinite; **(1 mark)**
2) Kaolinite can form from the weathering of smectite; **(1 mark)**
3) Highly weathered soils are acidic or at least less alkaline than soils that underwent intermediate weathering; **(1 mark)**
4) These soils also have a lower base status **(1 mark)** and low soluble silicon content; **(1 mark)**
5) Under abovementioned conditions kaolinite is the most stable phyllosilicate; **(1 mark)**
6) An abundance of ferric and aluminium (oxy) hydroxides are also expected, it is possible that kaolinite is metastable with respect to gibbsite under these conditions; **(1 mark)**
7) Kaolinite has a lower CEC compared to 2:1 clay minerals; **(1 mark)**
8) Variable charges are more dominant and minerals also have a greater affinity for anions (sign of positive charge). **(1 mark)**

<u>Intermediate weathering</u>
1) Soils are expected to be more alkaline with higher base status **(1 mark)** and also higher aqueous silicon concentrations; **(1 mark)**
2) Under these conditions smectites, for example, montmorillonite will be more stable; **(1/2 mark)**
3) A greater diversity of phyllosilicate minerals can possibly be stable depending on the base status of the soil **(1 mark):** Vermiculite **(1/2 mark)**, Hydroxy- interlayer vermiculite **(1/2 mark)**, Hydroxy- interlayer smectite (if soil acidifies a bit) **(1/2 mark).**
4) Permanent negative charge is dominant and minerals exhibit greater CEC than kaolinite; **(1 mark)**
5) Soils can exhibit swelling properties. **(1 mark)**

Question 3 / Vraag 3

Zinc (Zn) is an essential element for plants and increasingly included in fertilizers because it is believed that our soils are gradually being depleted of zinc. Its long term plant availability and environmental available (to leaching and reach water bodies) is a function of the mineral or minerals it transformed to. Willemite (Zn_2SiO_4) and Franklinite ($ZnFe_2O_4$) are two possible minerals which potentially can control Zn availability.

Sink (Zn) is 'n essensiële plantvoedingstof en word toenemend by kunsmis mengsels gevoeg omdat daar geglo word dat Zn in ons landbougrond opgebruik word. Die langtermyn plant beskikbaarheid en omgewings beskikbaarheid (vir die vervoer na bo- en ondergrondse water) is 'n funksie van die mineraal / minerale waarna dit transformeer. Willemiet (Zn_2SiO_4) and Frankliniet ($ZnFe_2O_4$) is twee moontlike minerale wat potensieel die beskikbaarheid van sink kan beheer.

3.1) Ignore solution complexation between silicon and Zn^{2+} furthermore, assume that Si activity is controlled by quarts and Fe^{3+} activity is controlled by goethite an calculate the solubililty of willemite and franklinite at pH 4 and 6. / *Ignoreer oplossingskompleksering tussen silikon en Zn^{2+} verder neem aan dat Si aktiwiteit word beheer deur kwarts en Fe^{3+} aktiwiteit word beheer deur goethiet en bereken die oplosbaarheid van willemiet en frankliniet by 'n pH van 4 en 6.* (12)

Franklinite

Assumptions
H_2O activity is unity
($\frac{1}{2}$) Mineral activity is unity
Activity = concentration

$$\frac{(Zn^{2+})(Fe^{3+})^2}{(H^+)^8} = 10^{4,81}$$

$$(Zn^{2+}) = (Fe^{3+})^{-2}(H^+)^8\,10^{4,81} \quad (\tfrac{1}{2})$$

However, goethite controls (Fe^{3+})

$$\therefore \frac{(Fe^{3+})}{(H^+)^4} = 10^{-2,21}$$

$$(Fe^{3+}) = (H^+)^4\,10^{-2,21} \quad (\tfrac{1}{2})$$

$$(Zn^{2+}) = \left[(H^+)^4\,10^{-2,21}\right]^{-2}(H^+)^8\,10^{4,81}$$

$$= (H^+)^{-8}\,10^{+4,42}(H^+)^8\,10^{4,81}$$

$$= 10^{+9,23} \quad (\tfrac{1}{2})$$

Hydrolysis species

$$ZnOH^+ = 10^{-7,69}(Zn^{2+})(H^+)^{-1} = 10^{+1,54}(H^+)^{-1} \quad (\tfrac{1}{2})$$

$$Zn(OH)_2^0 = 10^{-16,80}(Zn^{2+})(H^+)^{-2} = 10^{-7,57}(H^+)^{-2} \quad (\tfrac{1}{2})$$

$$Zn(OH)_3^- = 10^{-27,68}(Zn^{2+})(H^+)^{-3} = 10^{-18,45}(H^+)^{-3} \quad (\tfrac{1}{2})$$

$$Zn(OH)_4^{-2} = 10^{-38,29}(Zn^{2+})(H^+)^{-4} = 10^{-29,06}(H^+)^{-4} \quad (\tfrac{1}{2})$$

$$[Zn\,tot]_{aq} = [Zn^{2+}] + [ZnOH^+] + [ZnOH_2^0] + [Zn(OH)_3^-] + [Zn(OH)_4^{2-}]$$

$$= [10^{+9,23}] + 10^{+1,54}(H^+)^{-1} + 10^{-7,57}(H^+)^{-2} + 10^{-18,45}(H^+)^{-3} + 10^{-29,06}(H^+)^{-4} \quad (\tfrac{1}{2})$$

At pH 4:

$$= 10^{9,23} \quad (1)$$

At pH 6: $10^{9,72}$ (1)

Willemite   Question 3.1

$$\frac{(H_4SiO_4^{\circ})(Zn^{2+})^2}{(H^+)^4} = 10^{16,01}$$

$$(Zn^{2+}) = \left[(H^+)^4 (H_4SiO_4^{\circ})^{-1} 10^{16,01}\right]^{\frac{1}{2}}$$

$$= (H^+)^2 \cdot (H_4SiO_4^{0})^{-\frac{1}{2}} 10^{8,005} \quad \left(\tfrac{1}{2}\right)$$

Quarts control (Si)

$$(H_4SiO_4)^{\circ} = 10^{-4} \quad \left(\tfrac{1}{2}\right)$$

$$\therefore (Zn^{2+}) = (H^+)^2 (10^{-4})^{-\frac{1}{2}} 10^{8,005}$$

$$= (H^+)^2\, 10^{10,005} \quad \left(\tfrac{1}{2}\right)$$

Hydrolysis species

$$Zn(OH^+) = 10^{-7,69}\left[(H^+)^2 10^{10,005}\right](H^+)^{-1} = 10^{2,315}(H^+) \quad \left(\tfrac{1}{2}\right)$$

$$Zn(OH)_2^{\circ} = 10^{-16,80}\left[(H^+)^2 10^{10,005}\right](H^+)^{-2} = 10^{-6,795} \quad \left(\tfrac{1}{2}\right)$$

$$Zn(OH)_3^{-} = 10^{-27,68}\left[(H^+)^2 10^{10,005}\right](H^+)^{-3} = 10^{-17,675}(H^+)^{-1} \quad \left(\tfrac{1}{2}\right)$$

$$Zn(OH)_4^{2-} = 10^{-38,29}\left[(H^+)^2 10^{10,005}\right](H^+)^{-4} = 10^{-28,285}(H^+)^{-2} \quad \left(\tfrac{1}{2}\right)$$

$$Zn\ tot_{aq} = (H^+)^2 10^{10,005} + 10^{2,315}(H^+) + 10^{-6,795} + 10^{-17,675}(H^+)^{-1} + 10^{-28,285}(H^+)^{-2} \quad \left(\tfrac{1}{2}\right)$$

at pH 4   at pH 6

$10^{2,01}$ (1) $10^{-1,99}$ (1)

3.2) Which mineral do you expect to be the most stable at the respective pH values? / *Watter mineraal verwag jy sal die meeste stabiel wees by die onderskeie pH waardes ?* (2)

Willemite **(2 mark)**

3.3) Generally Zn levels in solution lower than 0.8 µ mol ℓ $^{-1}$ is considered insufficient for plants. When enough time is allowed for Zn containing fertilizer to react with the soil and the zinc transformed to its most stable mineral form, will this mineral be soluble enough to supply sufficient amounts of Zn to crops? / *In die algemeen word sink konsentrasies laer as 0.8 µ mol ℓ $^{-1}$ gesien as te laag om in die behoeftes van plante te voldoen. As daar genoeg tyd toegelaat word vir die kunsmis om te reageer met die grond en te transformeer na die stabiele mineraal /minerale* sal dit oplosbaar genoeg wees om aan die sink behoeftes van plante te voorsien. (1)

Yes, the solubility of Willemite is sufficient t **(1 mark)**

3.4) What management strategies will you employ to ensure maximum utilization of Zn by crops? / *Watter bestuurspraktyke sal jy toepas om die maksimum plant beskikbaarheid van sink te verseker?* (4)

1) Based on the Ostwald step rule, zinc should not be applied to soil long before crops are planted**; (1 mark)** 2) Zinc will transform to increasingly insoluble crystalline forms with time; **(1 mark)** 3) Neutral soil conditions will decrease Zn availability, best Zn utilization will be under conditions below 6; **(1 mark)** 4) Liming of soil should also carefully managed. Over liming will result in Zn deficiencies because of low mineral solubility; **(1 mark)** 5) Soil should also not allowed to acidify, although it can increase Zn mineral solubility, it can become toxic; **(1 mark)** 6) Complex soil reactions and precipitation of Zn by soil minerals can be circumvented through leave application of Zn; **(1 mark)** 7) Theoretically the application of organic ligand (humates and fulvates) will increase plant availability because of increase solution complexation and decrease precipitation. **(1 mark)**

3.5) You are an environmental consultant and called out to a site polluted with an acidic effluent rich in Zn. You have access to fly ash from a local power station and preliminary tests showed that applying a certain amount to the soil will increase the Si concentration in solution to 0.01 M and the pH to 7.5. On hand of appropriate calculations, do you think this could be an effective remediation strategy? *Jy is 'n omgewingskonsultant en word ontbied na 'n grond wat besoedel is met suur afval water ryk aan sink. Jy het toegang tot vliegas van 'n plaaslike kragstasie en voorlopige toetse het gewys as jy 'n sekere hoeveelheid by die grond gooi verhoog die Si konsentrasie in oplossing na 0.01 M en die pH na 7.5. Aan hand van gepaste berekening dink jy hierdie kan 'n effektiewe remediëring strategie wees?* (5)

Question 3.5

$$(Zn^{2+}) = (H^+)^2 (H_4SiO_4^0)^{-\frac{1}{2}}\, 10^{8{,}005}$$

If pH = 7,5 and assume $[Si_{tot}]_{aq} = [H_4SiO_4^0]$

$$(Zn^{2+}) = (10^{-7{,}5})^2 (10^{-2})^{-\frac{1}{2}} \cdot 10^{8{,}005}$$
$$= 10^{-5{,}995}$$

$$Zn(OH^+) = 10^{-7{,}67} [Zn^{2+}](H^+)^{-1} = 10^{-6{,}185}$$
$$Zn(OH)_2^0 = 10^{-16{,}80} [Zn^{2+}](H^+)^{-2} = 10^{-7{,}795}$$
$$Zn(OH)_3^- = 10^{-27{,}68} [Zn^{2+}](H^+)^{-3} = 10^{-11{,}175}$$
$$Zn(OH)_4^{2-} = 10^{-38{,}29} [Zn^{2+}](H^+)^{-4} = 10^{-14{,}285}$$

$[Zn_{tot}]_{aq} = 10^{-5{,}7745}$ versus $\underline{10^{-4{,}77450}}$ at pH=7,5 when quarts control (Si^{4+}).

willemite is therefore less soluble if pH is raised to 7,5 and (Si^{4+}) increased to 10^{-2}M.

<u>Franklinite</u>
$ZnFe_2O_{4\,(s)} + 8\,H^+_{(aq)} \leftrightarrows Zn^{2+}_{(aq)} + 2\,Fe^{3+}_{(aq)} + 4\,H_2O_{(l)}$ log K_1 = 4.81

<u>Quarts</u>
α -$SiO_{2\,(s)} + 2H_2O_{(l)} \leftrightarrows H_4SiO_4{}^0{}_{(aq)}$ log K_2 = -4.00

<u>Willemite</u>
$Zn_2SiO_{4\,(s)} + 4\,H^+_{(aq)} \leftrightarrows 2\,Zn^{2+}_{(aq)} + H_4SiO_4{}^0{}_{(aq)}$ log K_3 = 16.01

<u>Goethite</u>
$FeOOH(s) + 4\,H^+_{(aq)} \leftrightarrows Fe^{3+}_{(aq)} + 2\,H_2O_{(l)}$ log K_4 = -2.21

<u>Hydrolysis of Zn in solution</u>
$Zn^{2+}_{(aq)} + H_2O_{(l)} \leftrightarrows ZnOH^+_{(aq)} + H^+_{(aq)}$ log K_5 = -7.69
$Zn^{2+}_{(aq)} + 2H_2O_{(l)} \leftrightarrows Zn(OH)_2{}^0{}_{(aq)} + 2H^+_{(aq)}$ log K_6 = -16.80
$Zn^{2+}_{(aq)} + 3H_2O_{(l)} \leftrightarrows Zn(OH)_3{}^-{}_{(aq)} + 3H^+_{(aq)}$ log K_7 = -27.68
$Zn^{2+}_{(aq)} + 2H_2O_{(l)} \leftrightarrows Zn(OH)_4{}^{2-}{}_{(aq)} + 4H^+_{(l)}$ log K_8 = -38.29

<u>Silicon hydrolysis</u>
$H_4SiO_4{}^0{}_{(aq)} \leftrightarrows H_3SiO_4{}^-{}_{(aq)} + H^+_{(aq)}$ log K_9 = -9.71
$H_4SiO_4{}^0{}_{(aq)} \leftrightarrows H_2SiO_4{}^{2-}{}_{(aq)} + 2H^+_{(aq)}$ log K_{10}= -22.98