Adsorption Behavior of HAu^*Cl_4 a Generic Adsorbing Tracer

(For finding wetting behavior of fluids in oil and gas industry)

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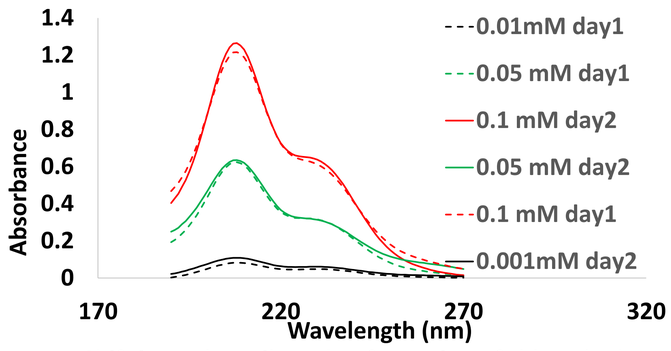
Abstract

Tracers are widely used to study flow behaviour in porous media. Dual tracer method, which uses one adsorbing tracer and one non adsorbing tracer, is used to characterize the porous media for wetting efficiency of the fluid in gas liquid reactors (trickle bed reactor), oil reservoirs. Non-adsorbing tracers are well studied in the literature. Chloroauric acid ($HAuCl_4.3H_2O$), with Au-198 as gamma emitter, is a tracer that adsorbs on the solid surface. It is adsorbed on the surfaces that are easily protonated like silicates (albite, quartz, feldspar), chitosan, polymers and a wide variety of surfaces. This adsorbing behaviour makes chloroauric acid a potential generic adsorbing tracer for oil and gas industry. Silica gel is used in lab scale reactor experiments to form a porous medium. Therefore, adsorption kinetics and dynamics of chloroauric acid on glass surface will impact the characterization of the porous media using the two tracer technique. In the present work, adsorption of chloroauric acid on silica gel is studied. Non-radioactive form of chloroauric acid is used for this study which can be translated to radioactive gold chemical for better accuracy at industrial scale.

Challenges in UV-Vis Spectrophotometry



- $HAuCl_4$ in double distilled water is used at different concentrations
- The UV –Vis spectrum shows day-wise variation
- Shift in peak attributed to formation of chloro-hydroxo complexes in concentration <0.1mM* (oxidation of gold tracer by ions)

  $Au(Cl)_4^- + OH^- \rightarrow Au(OH)Cl_3^- + Cl^-$

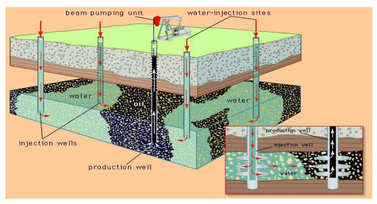
  $Au(OH)Cl_3^- + OH^- \rightarrow Au(OH)_2(Cl)_2^- + Cl^-$
- Addition of NaCl should reduce the oxidation

  $NaCl + Au(Cl)_2(OH)_2^- \rightarrow Au(Cl)_3(OH)^- + Na^+ + OH^{-**}$

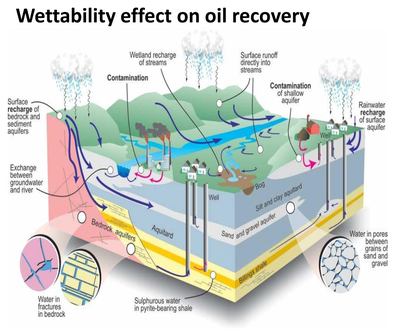
*., Peck, J. A., Tait, C. D.,Swanson B. I.,Brown, J.E., "Speciation of aqueous gold(II1) chlorides from ultraviolet/visible absorption and Raman/resonance Raman spectroscopies"*Geochimica et Cosmochimica Acta* ,55,. 671 (1990)

** Murphy, P. J., Stevens G., LaGrange M.S., "The effects of temperature and pressure on gold– chloride speciation in hydrothermal fluids: A Raman spectroscopic study "*Geochimica et Cosmochimica Acta,* 64,479 (2000)

Uses of Adsorbing Tracer



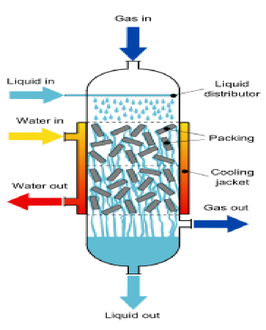
Wettability effect on oil recovery

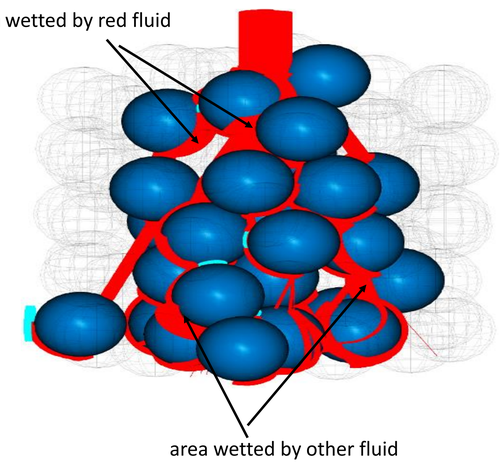


Contaminants flow path determination in aquifers

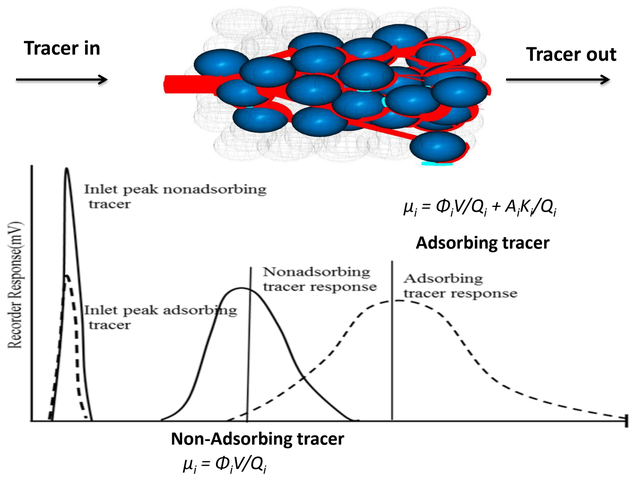
http://www.cgenarchive.org/ottawa-gatineau-groundwater.html

Multiphase reactors





How to Quantify Wetted Area

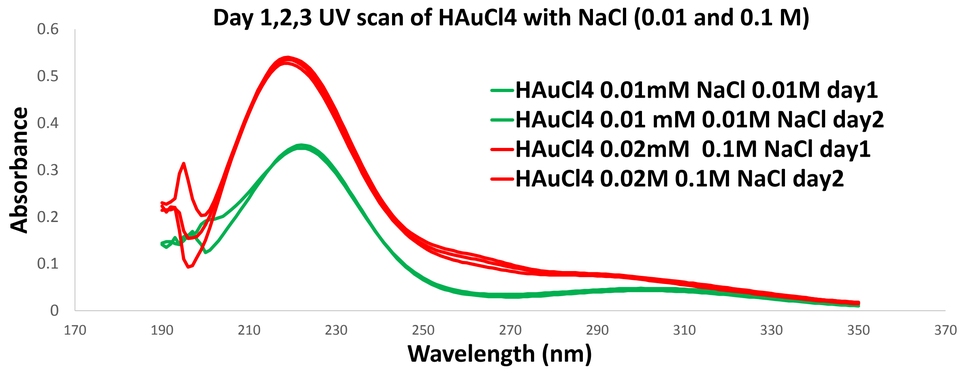


- Wetted area can be estimated by dual tracer experiment
- Adsorption coefficient Ki is needed

Silica gel is chosen as substrate and HAuCl4 as adsorbing tracer

Addition of NaCl

Day 1,2,3 UV scan of HAuCl4 with NaCl (0.01 and 0.1 M)



- Addition of NaCl stops degradation of $HAuCl_4$
- NaCl 0.1M gives same absorbance of gold tracer for three days

pH of Silica gel/glass in Water

Adsorbent used	Initial pH	Final pH	Time of aging	Reason
Glass beads	DI water pH=7	8.8	10 min–10hours	Na^+ in glass replaced by H^+ of water
Glass beads	HCl (400mM) pH 1– 0.5	7	~ 1 day	Not suitable for adsorption, acidic pH needed
Glass beads	HCl (2M) < pH 0.5	1.5	~ 12 days	Such low pH can be maintained in experiment but not in reservoir
Silica gel	DI water pH = 7	8.13	4 hrs	Improvement required
Silica gel	HCl (0.1mM) pH 4-6	~7	24 hrs	Improvement required
Silica gel	HCl (10mM) pH 2-3	~4	24 hrs	Suitable for adsorption

So, silica gel is chosen as adsorbent with 0.01M HCl and 0.1M NaCl

$HAuCl_4$ adsorption on silica gel

Silica gel as substrate

- Silica gel layer forms on the aluminosilicates found in oil reservoirs and gold ores in acidic medium*
- Has less impurities and controlled experiments in lab can be done
- Can be made oil wet during experiments for oil reservoirs

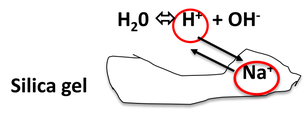
$HAuCl_4$ as adsorbate

- HAuCl4 can be used as a generic adsorbing tracer for many materials
- Can be used as a water phase tracer
- Can be made radioactive for very small concentration detection

Challenges

- Difficult to use the radioactive form in lab, chemical detection of HAuCl4 needed
- Adsorbs only in acidic medium
- HAuCl4 may degrade in water

- Na^+ ions in Silica gel consumes H^+ ions in aqueous solution making it basic **



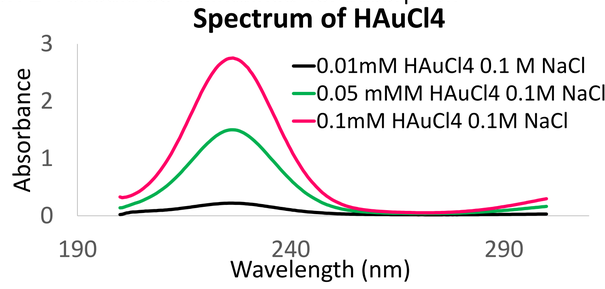
*Feng, D.,. Provis, J.L., van Deventer, J. S. J., " Adsorption of gold on albite in acidic chloride media", *Hydrometallurgy* 134–135, 32 (2013)

**Allent, L. H., Matejevic E., Meites, L., "Exchange of Na+ for the silanolic protons of silica "Journal of Inorganic Nuclear Chemistry", 33, 1293 (1971)

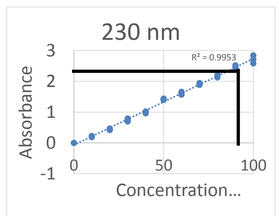
Calibration

- To conduct measurements using spectrophotometry HAuCl4 tracer should be stable
- pH 2-4 should be maintained for adsorption

Spectrum of HAuCl4



Linear Calibration



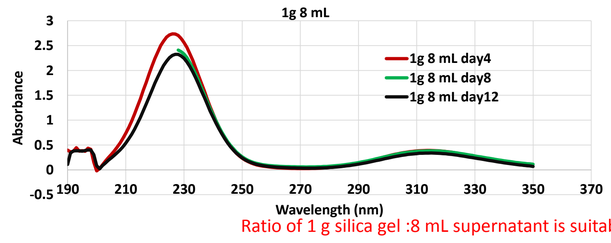
As silica gel is a substrate and will be used in adsorption experiments, to get the base solution silica gel is aged in DD water for 5 hours, then the water is made 0.1M NaCl and 0.01M in HCl and aged with silica gel for 24 hours. The supernatant thus obtained is used for UV-Vis spectrophotometer calibration of HAuCl4 concentration.

Adsorption Quantification

- Too little or too much adsorption cannot be quantified using spectrophotometer
- Solid silica gel weight : volume of liquid supernatant is found by ratio scope in experiments

Different samples each of certain Solid silica gel weight : supernatant volume are prepared (aging with DD water for 5 hrs, Adding NaCl and HCl, ageing for 24 hrs, addition of HAuCl4 adsorbing tracer, spectrophotometer reading for 12 days , once each day)

- **1gm : 8 ml of silica gel and water ratio will be used for adsorption experiments as shown in below**



Initial conc:100 μM
After 4 days: 92 μM
Final conc:69μM

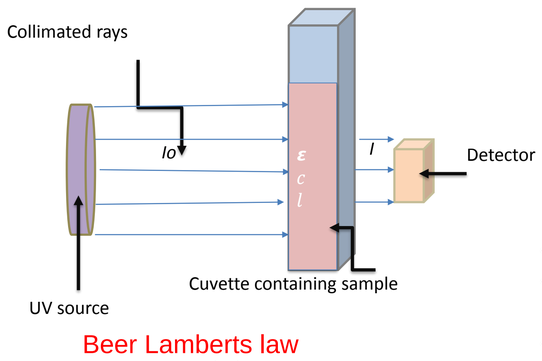
Ratio of 1 g silica gel :8 mL supernatant is suitable

Next Step $\mu_i = \Phi_i V/Q_i + A_i K_i/Q_i$

- To find out Ai (area of contact), Ki (adsorption coefficient) is to be measured for Gold tracer adsorption on silica gel
- Adsorption isotherms will be obtained
- If required adsorption kinetics have to be considered for flow experiments

UV-Vis Spectrophotometer for Non-radioactive Tracer in Lab

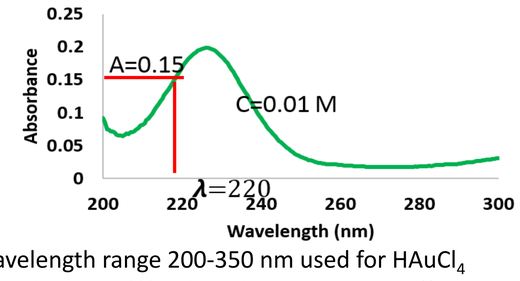
Detection of tracer is done using UV spectrophotometry



Beer Lamberts law

$$A = log_{10}\left(\frac{I}{Io}\right) = \varepsilon cl$$

Absorbance vs Wavelength



- Wavelength range 200-350 nm used for $HAuCl_4$
- Absorbance vs Wavelength measured at different concentrations
- Linear relation between absorbance and concentration can be found