ExxonMobil’s Approach to In Situ Co-Development of Oil Shale and Nahcolite

J. D. Yeakel, W. P. Meurer, R. D. Kaminsky, W. A. Symington, M. M Thomas
Oil Shale or Nahcolite: Which to Choose?

Oil Shale

Nahcolite
Oil Shale or Nahcolite: You Can Have Both

Oil Shale

Nahcolite
Nahcolite & Oil Shale Are Valuable Resources

**Oil Shale**

400 Billion Barrels Shale Oil

**Nahcolite**

32 Billion Short Tons

*Recoverable Quantities of Shale Oil and Nahcolite Are Not Well Defined*

*Resource Values from Pitman et al. (1989) and Dyni (1974)*
ExxonMobil Process can Recover both Shale Oil and Sodium Minerals

• Heat oil shale *in situ*, for example with Electrofrac™ electrically conductive fractures
  – Will preserve sodium mineral value
  – Enhance porosity and permeability
• Produce oil and gas
• Water flood to recover residual hydrocarbons and sodium minerals
• In situ pyrolysis followed by nahcolite recovery patent pending
Outline

• What is Nahcolite?
• Mode and Occurrence of Nahcolite
• ExxonMobil Concept for Recovery of Nahcolite and Oil Shale Value
  – Preservation of Sodium Mineral Value
  – Enhanced Porosity and Permeability
What is Nahcolite?

- Nahcolite = NaHCO₃
- Natural form of baking soda
- Chemically related minerals include:
  - Natrite (Na₂CO₃)
  - Thermonatrite (Na₂CO₃·H₂O),
  - Trona (Na₃H(CO₃)₂·2H₂O),
  - Natron (Na₂CO₃·10H₂O)
- First identified in a lava tunnel at Mount Vesuvius
- Readily soluble in water
Nahcolite Present in Several Forms

Nahcolite occurs as:

- Nonbedded crystalline aggregates
- Finely disseminated crystals in oil shale – laterally continuous units
- Brown microcrystalline beds
- White coarse-grained beds

Using Conventional Solution Mining Recovery Methods

- Bedded nahcolite more easily recoverable
- Crystalline aggregates and disseminated crystals difficult to recover due to kerogenous oil shale matrix

Photos from USGS Prof. Paper 1310 (1987)
ExxonMobil Concept Will Preserve Sodium Value & Increase Porosity & Permeability

**Phase I: Drill wells, place fractures begin heating**

**Phase II: Heating causes conversion of kerogen to oil and gas**

Nahcolite partially altered to other water soluble sodium minerals (sodium carbonates).

Kerogen conversion fractures heated and unheated rock, increasing porosity & permeability.
Sodium Mineral Value Preserved

Theoretical

• As temperature increases nahcolite breaks down to form natrite and/or trona
  – \(2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2\)
  – \(5\text{NaHCO}_3 \rightarrow \text{Na}_3\text{H}((\text{CO}_3)_2 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 + 2\text{CO}_2\)
  – \(3\text{NaHCO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_3\text{H}((\text{CO}_3)_2 \cdot 2\text{H}_2\text{O} + \text{CO}_2\)

• Both natrite and trona are highly water soluble

• At very high temperatures (> 800 °C) natrite breaks down to form disodium oxide
  – \(\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2\)
Nahcolite Will Be Converted to Soda Ash

- Majority of rock heated by *in situ* methods will be at temperatures of 400-700 °C
- Carbon dioxide fugacity will be high due to:
  - Conversion of nahcolite to natrite
  - Conversion of kerogen to hydrocarbons
- Carbon dioxide fugacity will remain high even at higher than process temperatures
  - Breakdown of calcite and dolomite
- Majority of heated nahcolite will be converted to natrite (soda ash)
  - Soda ash is water soluble
  - Soda ash can be readily converted to nahcolite by CO₂ addition
  - Soda ash stable to 1000 °C as either solid or liquid at high CO₂ concentrations
Starting materials include both homogeneous mixes and sandwiches of pure nahcolite and oil shale.

Mixtures heated to 375 and 393 °C for 24 hours in Parr vessel

Run products show:
- Some nahcolite preserved
- Conversion of nahcolite to natrite and trona
- Absence of Na₂O
Experimental Results Verify Sodium Value Preserved

- No Na$_2$O generated
- Nahcolite is not entirely converted to natrite in mixed experiments
- At 393 ºC in sandwiches nahcolite converts to a mixture of natrite and trona
- Mixed experiments suggest that oil shale may retard the breakdown of nahcolite
Volume Expansion Due to Kerogen Conversion

1 Ton of Green River Oil Shale (22% TOC, 42 gal/ton)

Before Conversion
- 8.1 ft³ kerogen
- 8.4 ft³ mineral
- 16.5 ft³ total

After Conversion @ 2400 psi, 750ºF (without liquid cracking to gas)
- 2.9 ft³ coke
- 9.4 ft³ HC vapor
- 6.6 ft³ HC liquid
- 27.3 ft³ total

Experiments Show Porosity Enhanced Even Under Lithostatic Stress

Unreacted Sample

Unstressed (375 °C)

Stressed (375 °C)

Berea sandstone sleeve & caps

Oil shale plug

Very Low Porosity

Abundant Macro Porosity

Numerous Micro Fractures and Pores
ExxonMobil Hydrocarbon & Sodium Mineral Recovery Concept

Phase III: Main Stage of Hydrocarbon Recovery

- Kerogen converted to oil and gas
- Oil and gas flow to production wells
- Nahcolite altered to trona and natrite
- Porosity and permeability increase due to kerogen conversion and volume loss

Phase IV: Post-Heating Recovery and Environmental Restoration

- Volume allowed to cool
- Some production wells converted to water injection wells
- Water circulated through subsurface
- Residual hydrocarbons recovered
- Sodium minerals recovered
- Environmental restoration completed
Summary of ExxonMobil Concept for *In Situ* Recovery of Shale Oil and Nahcolite

Phase I: Drill wells, place fractures, begin heating

Phase II: Early heating, kerogen conversion, shale oil migration, porosity development

Phase III: Full heating, primary shale oil production, nahcolite conversion to natrite / trona

Phase IV: Cooling, water flood, nahcolite recovery, environmental restoration

Patent Pending
Conclusions

• Nahcolite and Oil Shale can be Co-Developed
• Oil Shale Development Should Proceed First
  – Enhanced porosity and permeability
  – No decrease in sodium mineral value
• Nahcolite Recovered by Water Injection after Primary Hydrocarbon Recovery
  – Coincident with residual oil recovery and environmental restoration