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Separation of CO_2 from Flue Gas and Potential for Geologic Sequestration

(Report prepared in 2002 for Tennessee Valley Authority)

By

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SUMMARY

The objectives of this study were to review various methods reported in the literature for the separation and geologic sequestration of carbon dioxide and evaluate the potential of TVA fossil fuel-burning plant locations for onsite geologic sequestration of CO_2 from stack emissions.

Several conventional and nonconventional technologies for the separation of CO_2 from flue gas, including absorption, adsorption, cryogenic distillation, membranes, hydrate formation and dissociation, and ammonia carbonation, have been reviewed in terms of separation mechanisms, flow diagrams, and costs. Most of the technologies that have been reviewed are still at the research and development stage. Critical information needed to assess and compare these technologies is still lacking. In addition, information on some of the technologies that have been tested at a pilot or industrial scale has not been fully disclosed in the open literature. Because of this lack of data, it is difficult to make a critical assessment of each of the separation technologies. Based on limited information, it was concluded that the most promising methods are membrane separation and the Mitsubishi process for chemical absorption. Both processes involve separating CO_2 at high temperature, minimizing the cost for cooling prior to separation.

Physical and chemical geologic formations of CO_2 were also reviewed. It was concluded that due to the geologic time scale of CO_2 sequestration periods, relatively safe conditions, general proximity to CO_2 sources, and extensive knowledge of underground conditions, sequestration of CO_2 in underground aquifers and coal beds is a very promising method of mitigating greenhouse gas emissions. The cost is predicted to be relatively low and the suitable sites are numerous for this application, with many of these sites located close to the plants.

Several TVA fossil fuel-burning plant locations including the Shawnee and Paradise plants in Kentucky; the Allen, Johnsonville, Cumberland, Gallatin, Kingston, Bull Run, and John Sevier plants in Tennessee; and the Widows Creek and Colbert plants in Alabama were evaluated for onsite geologic sequestration of CO_2. The suitability of a site for deep CO_2 injection was evaluated based on the following criteria:

1. Basin origin and tectonic setting
2. Regional scale geology, lithology, and hydrostratigraphy
3. Known oil, gas, and coal reserves.
4. Depths to the 32° C isotherm and 7.4 MPa isobar
5. Hydrodynamic regime
6. Permeable and porous zones for injection and sequestration
7. Economic considerations (e.g., potential for hydrocarbon recovery, existing infrastructure)
8. Socio-political considerations
9. Availability of data

Criteria 1-8 have been suggested in the literature and the ninth criterion was added in recognition of the wide variation in data that is readily available for site evaluation. Where very little information is available, there is a risk involved in the investment of time and resource on detailed site characterization in the absence of a strong indication that sequestration potential exists.

The following table lists the TVA fossil plant locations in order of greater to lesser suitability as potential CO_2 sequestration sites:

TVA fossil plant sites ranked according to suitability for CO_2 sequestration.

Plant	Rating	Comments
Paradise	Very Good	Best candidate due to favorable geologic characteristics and wealth of available data. Potential use of existing well infrastructure. Potential for multiple targets (brine formation, oil or gas reservoir, or coal bed storage).
Johnsonville	Very Good	Favorable geology for underground storage and availability of deep well data. Favorable location within deep groundwater flow system.
Gallatin	Favorable	Favorable geologic characteristics, although detailed subsurface geology is less well known.
Allen	Marginal	Insufficient data to fully evaluate potential targets at depth. Reasonable candidate for additional evaluation if primary choices are found unsuitable. Long transport pathways to potential discharge locations.
Kingston	Marginal	Favorable formations at depths below the Chattanooga Fault, but deep disposal is required. Shallower horizons are complexly faulted.
Widows Creek	Marginal	Limited data, but underground structural complexity is likely based on location in the Appalachian fold belt.
Colbert	Potential	Potentially favorable geologic characteristics based on tectonic setting. However, subsurface data not available to evaluate the potential as good or poor.
Shawnee	Poor	Unfavorable geology for underground storage. Low priority for additional evaluation.
John Sevier	Poor	Underground structural complexity.
Bull Run	Poor	Significant vertical faults at and near the plant and steeply-dipping stratigraphy.
Cumberland	Poor	Marginal depth for injection at supercritical conditions. Complex structure associated with impact crater. Permeability of faults could be conduit for CO_2.

The sites that are given the highest priority for further evaluation as CO_2 injection test sites are the Paradise Fossil Plant in Muhlenberg County, Kentucky, and the Johnsonville fossil Plant in Humphreys County, Tennessee. The Paradise site has potential for sequestration in any or all of coalbeds, saline reservoirs, and depleted oil or gas reservoirs. The Johnsonville site would be restricted to saline reservoir sequestration. Both have deep well information available. In both areas, issues of permitting and regulatory acceptance are likely to be eased by previous or ongoing activities – hydrocarbon production in the case of the Paradise site, and deep hazardous waste disposal in the case of the Johnsonville site. Both show evidence of porous and permeable zones at a depth that is sufficient for supercritical CO_2.

Additional work is required to obtain the detailed data necessary to further evaluate these sites. It may be necessary to establish contact with site owners where drilling operations have been conducted in order to obtain welltest data and borehole logs. However, this preliminary investigation indicates that both of these sites have good potential.

I. SEPARATION OF CO_2 FROM FLUE GAS

Introduction

Separations methods for CO_2 from flue gas is a current subject of research and development. Methods that are investigated include absorption using solvents or solid sorbents, pressure- and temperature-swing adsorption using various solid sorbents, cryogenic distillation, membranes, and other novel and emerging technologies. These methods are reviewed in this section.

Absorption

The process of CO_2 absorption by a liquid solvent or solid matrix is currently being investigated for scrubbing CO_2 from flue gas streams. Absorption is a process that relies on a solvent's chemical affinity with a solute to preferably dissolve one species over another. In CO_2 absorption processes, a solvent is used that dissolves CO_2, but not oxygen, nitrogen gas, or any other components of a flue gas stream. The CO_2-rich solution is typically pumped to a regeneration column where the CO_2 is stripped from the solution and the solvent recycled for a new batch of flue gas. The absorption equipment should be placed after the flue gas desulfurization (FGD) step and before the stack. Optimal conditions for absorption are low temperature and high pressure, making this the best location for absorption to occur. In addition, most solvents are easily degraded by compounds such as fly ash, other particulates, SO_x (SO_2, SO_3, and SO_4) and NO_x (NO_2 and NO_3), so the absorption step must take place after electrostatic precipitation (ESP) and FGD. In a typical absorption process, the CO_2-lean flue gas is either emitted to the atmosphere or possibly used in other applications (e.g., chemical production).

Monoethanolamine (MEA) Process

An effective, economical, and traditional solvent that can be used for CO_2 absorption is monoethanolamine (MEA). The flue gas from a fossil fuel power plant is passed through a column in which MEA selectively absorbs CO_2 (Figure 1). This CO_2-rich solution is then pumped to a tower in which thermodynamic conditions are manipulated to release the CO_2. High pressure and low temperature favor absorption while low pressure and high temperature result in regeneration of the solvent. The pressure in absorption systems can be atmospheric or can be manipulated (as explained above) to enhance absorption/desorption. Temperature manipulation (specifically, to release the CO_2 and regenerate the MEA) makes up 70-80% of operating cost. The main area of improvement for this process is finding a new solvent or refining the existing method to minimize regeneration conditions[1].

In Figure 1, the flue gas is cooled prior to entering the absorption chamber. The temperature should not go below the condensation point of the gas; therefore the minimum temperature should be above the condensation point of the gas and the solvent's freezing point. After absorption, the CO_2 rich solution is passed through a heat exchanger to

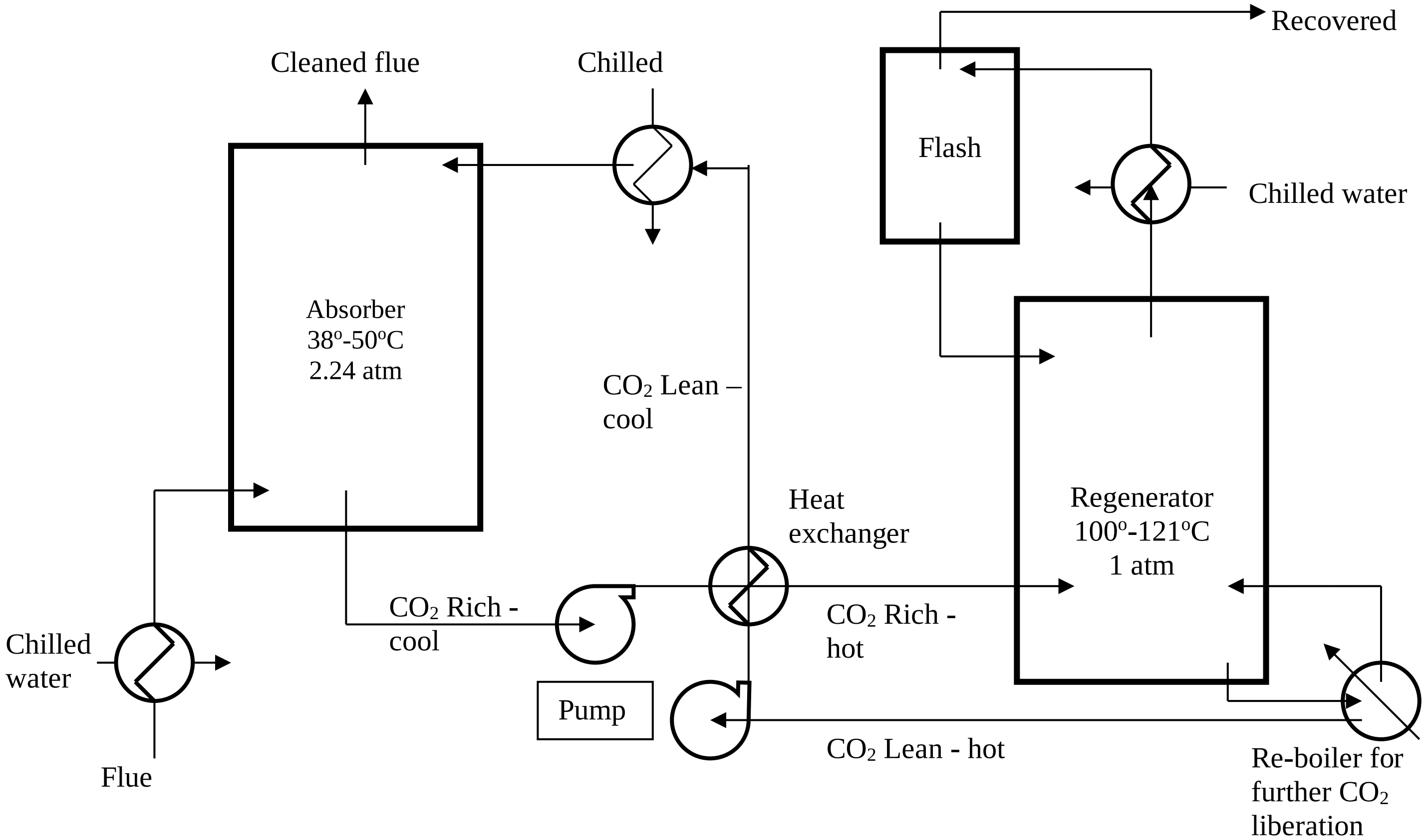


Figure 1 - Typical chemical absorption system[2].

recover some of the heat from a hot stream coming from the regenerator. It then goes into the regenerator and is heated to release the CO_2 in solution (if pressure is involved, the pressure is lowered). The CO_2-lean solution is then pumped back into the absorber for reuse (reusing solvent allows cost reduction; it has no bearing on performance of the solvent unless the solvent degrades with heating or is partially regenerated). The CO_2 liberated in the regenerator goes through a flash chamber where any water or other contaminants are removed, and the clean CO_2 gas stream is collected for storage or sequestration. There are many points where a chilled water stream exchanges heat with a solvent stream; this heat exchanging is a cost-effective method to conserve heat[2]. Some small amount of refrigeration is necessary to reduce the temperature of the cold water streams.

The absorption process has many design issues that it must overcome. The most important is regenerability of the solvent (regardlesss of the solvent, the process is the same). Since it is desirable to carry out the process with as little energy penalty as possible, the solvent activity must have an optimum balance between absorption and desorption rates. Absorption of CO_2 at low temperatures (35^o – 50^oC) and relatively low CO_2 partial pressure (proportional to concentration) can occur if the solvent is highly attracted to the solute, but this high attraction between the solvent and CO_2 causes regeneration energy to be high. If the solvent isn't very attracted to CO_2, regeneration is simple, but little loading is possible.

Another concern is oxygen content of the flue gas. High oxygen concentration can corrode carbon steel facilities and cause excessive amine loss. Hindered amines offer some resistance against degradation of the solvent. Acidic gases, such as SO_x, are also a major concern. It is preferable to keep levels of these gases below 0.001% because they form stable salts with the amines used for absorption. A SO_x scrubber is generally more cost-effective than purchasing more solvent to account for the losses. However, since typical SO_x scrubbers only remove 90% of the SO_x in the flue gas, degradation of solvent will be a major issue if MEA is used. Fly ash and NO_x compounds (any amount of any of these components will cause at least some degradation) create the same problems as SO_x compounds. Finally, the high temperature (at least 100^oC, higher than the maximum ideal temperature for MEA at 45^oC) associated with flue gases can degrade solvents and lower the solubility of CO_2. The temperature needs to be decreased to approximately 45^oC in the SO_x scrubber upstream from the separation column[3].

The greatest advantage of absorption is that there are solvents that can be easily regenerated. MEA has been used for over 60 years[4] in the chemical industry, while new solvents operating on the same principles are currently being investigated. This is a well-established method of separating CO_2 and the mechanisms and involved thermodynamics are well known. The fact that CO_2 absorbers can be regenerated is possibly the most attractive feature that motivates renewed research efforts focused upon improvement of the absorption process.

Advantages and Disadvantages to Absorption

When the CO_2-rich solution is sent into the regenerator, the solvent can be recycled, thus reducing the cost of material (as opposed to replacing the solvent for each absorption step). However, different conditions demand different solvents. For low partial pressures of CO_2 (< 15 vol. %), liquid solvents like MEA are preferable. For high partial pressures of CO_2 (> 15 vol. %), solid solvents, such as lithium hydroxide and lithium zirconate, are better because they can absorb more CO_2 and are more easily regenerated[5]. Also, the separated CO_2 stream from the regeneration column is of high purity. An exact percentage is not reported, but most absorption processes deliver a stream with purity higher than 95%. This is pure enough for sequestration. Another advantage offered by absorption is the non-dependence on human operators. Continuous monitoring and automation minimize human duties to addition of amine solvent and inhibitors. Thus, proper instrumentation and surveillance[3] minimize labor cost. Yet another advantage to chemical absorption is that it is so well known, and promising new solvents are already being pilot-tested by two separate companies.

While absorption does have strong advantages, the total cost (including addition of new solvent and other operating and maintenance, O&M, costs) is relatively high, about \$40 - \$70/ton CO_2 separated, as reported by Chakma *et al*[6]. The exact life of a batch of solvent was not reported for MEA or any other solvent, but solvent generally degrades before it replaced. The energy penalty of the entire absorption process (no O&M costs included) is approximately 0.155kWh/lbm CO_2 (\$13.95/ton CO_2), as reported by Gottlicher *et al*[7]. These two costs are not the same, however. The cost reported by Gottlicher is only the energy penalty necessary to operate the process. The cost reported by Chakma includes the cost of purchasing new solvent and other operational costs. Neither estimate includes capital and installation costs.

In addition to high regeneration costs, sulfur compounds (SO_x gases) present in flue gases during absorption degrade the solvents currently considered for absorption; approximately 3.5 lbm of solvent are lost for each ton of CO_2 separated[3]. Lost solvent is in the form of salts that do not dissociate in solution; they precipitate out. This phenomenon motivated the development of hybrid systems in which absorption is one of two or more processes used in synergy for CO_2 separation. When absorption is part of a hybrid system, the cost needed for replacing the degraded solvent is lower. The trace gases that are separated (NO_x, SO_x, O_2, and others) are either stored or reacted with other compounds to neutralize their harmful effects.

Improvement is necessary for absorption to be a possibility for CO_2 separation in the future, such as the new PSR™ solvents. They are a family of solvents being developed by a private company that require less heating for regeneration and are able to absorb more CO_2 than MEA. These solvents absorb 20-80% more CO_2 than MEA per unit volume of solvent, which allows them to be circulated more slowly through the system. Since MEA is not as efficient as a PSR solvent, it must be circulated more rapidly through the absorption system to remove the same volume of CO_2; this uses more energy. PSR solvents are also more resistant to degradation from flue gases and cause less corrosion of equipment[1]. The developer did not indicate whether the PSR solvents are being pilot tested or if they are still at the bench-scale testing stage.

Possibly the most promising absorption process is based on the KS-1, KS-2, and KS-3 solvents being developed by Mitsubishi Heavy Industries (MHI). This family of solvents shows higher CO_2 loading per unit solvent, lower regeneration conditions, and almost no corrosion, degradation, or amine loss. A novel packing material, KP-1, has also been developed that will further improve this process. Development has reached the pilot plant test stage[8] at MHI.

In addition to the Mitsubishi process, the Econamine FG™ process (FG is the title given by the authors; it may stand for Flue Gas) also shows lower overall costs (including O&M). This process improves upon regular MEA absorption by using hindered amines. Hindered amines are similar to regular amine solvents, but specific functional groups are bonded to these solvents that help defend against degradation. This lowers steam costs for regeneration, thereby lowering overall cost. Currently, the Econamine FG process costs $18.70/ton CO_2 in O&M costs when CO_2 is 13% of the flue gas by volume. It is being modified to further decrease the cost[3].

Flue Gas Desulfurization

One recent method that has been studied uses the separated SO_x compounds to form a solvent that absorbs CO_2. Laboratory experiments show that up to 2 ft^3 CO_2 / lb of flue gas desulfurization (FGD) product can be absorbed. Limestone based compounds are being used to separate SO_x from flue gas streams prior to absorption. These compounds are then slurried, becoming the solvent for absorption[9]. An attractive feature to this design is that many coal power plants already have FGD units equipped; some small amount of additional transport equipment for the slurry to be moved to the absorber would be necessary, minimizing capital cost for retrofitting an existing plant.

Other Possible Solutions

Another approach is to find better methods for insuring that maximum interaction takes place between the solvent and the flue gases. In a recent experiment[2], a column with gases and conditions typical of flue gases entering an absorption chamber was packed with different materials such as BX gauze, Flexipac, and intalox saddle. The packing in the saddle was either random or structured. Absorption took place at approximately 50°C for the MEA, regardless of which packing was used. Regeneration took place at 120°C, similar to the conditions shown in the Figure 1. This process is often used in current applications at most plants with MEA scrubbers. The structured packing showed the greatest solvent utilization at 43.9 ±0.5 % (fraction of solvent that absorbed CO_2), while the random packing had only 28.6% utilization. Structured packing involves a certain structure (not specified) to packing the material in the column; random packing involved a random structure to the packing material. Both cases relied on the principle that packing increased the surface area of the solvent, allowing for more interactions with entering gases, decreasing residence time[2].

Another improvement can be made by diluting the MEA solution with organic solvents, such as alcohols, instead of water. The concept is that if the organic solutions have lower heat capacities, the heat of regeneration should be decreased, thus reducing the energy penalty for regeneration. However, while adding methanol to MEA (instead of water) did not significantly decrease the absorption rate, a large amount of methanol evaporated while heating the solution. Thus, methanol is not suitable for regeneration at atmospheric pressure, but could be used in high-pressure systems such as the Integrated Gasification Combined Cycle (IGCC). Finding other organic solvents for MEA would be useful for regeneration at atmospheric pressure[2].

Solid Sorbents

Solid absorbents, such as calcium and lithium hydroxides, are also being investigated for use in CO_2 absorption. The temperatures associated with solid sorbents is usually much higher (~800°C for absorption and 1000°C for desorption), but the absorption rates are relatively fast; 50% absorption can achieved within one hour, and the absorbent can be totally regenerated in 15 min. In tests[10], the absorption rate dropped off after one hour, probably due to an impermeable build-up of $CaCO_3$ on the surface of the packed beds. Since $CaCO_3$ is a stable mineral, masking of the sorbent could occur, inducing costs for cleaning the sorbent surfaces. These sorbents function by the same mechanisms as wet solvents.

Solid absorbers have similar advantages and disadvantages as wet absorbers. Improving on existing systems is most possible by finding a new material that is more readily regenerated and less prone to degradation[1]. The treatment of the sorbents (to remove $CaCO_3$ deposits, possibly by acid washing) must be investigated to determine whether physic-sorption is a viable process.

In summary, different packing materials and organic solvents have various effects on the absorption rate and regeneration energy for the system. The right combination of solvent, packing, and conditions could yield a process that cleans flue gases for a fraction of the current costs. A list of materials and conditions reported thus far for the separation of CO_2 by absorption is given in Table 1.

Table 1. Materials and Conditions used in CO_2 Process

Absorbent	Absorption Temp (°C)	Absorption Pressure (atm)	Desorption Temp (°C)	Desorption Pressure (atm)	Cost ($/ton CO_2)
MEA	50	2.24	120	1	13.9
MEA (with Fe)	55	1	120	1	None reported
PSR	50	2.24	110	1	None reported
K_2CO_3	45	1	55	0.15	None reported

Adsorption

Adsorption is another method that can be used to separate CO_2 from flue gases generated by fossil fuel power plants. While absorption involves dissolution of CO_2 into the solvent, adsorption is a heterogeneous process. Due to interactivity between sorbent and guest molecules, CO_2 molecules are attracted and trapped by surface groups of the sorbent or physi-sorbed. Conditions can be manipulated that facilitate adsorption or desorption. Flue gases typically contain N_2, CO_2, H_2O, NO_x, SO_x, CO, O_2 and particulate matter when entering the stack, with concentrations varying depending on the location of the sampling point[11]. Many solids have the capability to selectively adsorb CO_2 into small cracks, pores, or just their external surfaces under specific temperature and pressure conditions. Adsorption can be performed on naturally occurring substances such as coal (a method of sequestering CO_2 in coal seams that cannot be mined) or more complex human-made sorbents such as activated carbon, molecular sieves, and zeolites.

The two main methods for adsorption are pressure swing adsorption (PSA) and temperature swing adsorption (TSA). In either case, adsorption rates depend on temperature, partial pressures of CO_2, surface forces (interaction energy between sorbent and CO_2), and pore size or available surface area of the sorbent[12]. It has been established that PSA is superior to TSA due to its lower energy demand and higher regeneration rate[13].

There are other methods for adsorption as well, one of the most promising being electrical swing adsorption. In this method, CO_2 is adsorbed onto a molecular sieve and then an electric current is passed through the sieve to efficiently release the CO_2[14]. Although the mechanism of electrical desorption is not well understood, it is believed that it is due to local temperature increase caused by the electrical current (this method is treated further below).

Figure 2 shows an example of a typical single chamber adsorption system. Flue gases enter the adsorption chamber after being cooled (Stage 1). This brings the temperature of the gases down from the flue gas temperature to the desirable 30°C. The chamber is pressurized by flue gas with compressors to maximize adsorption of CO_2, while the rest of the components of the flue gas are allowed to exit the chamber. A vacuum can then be applied to liberate the CO_2 from the sorbent (Stage 2). This gaseous CO_2 can then be sent via a separate outlet for sequestration[12].

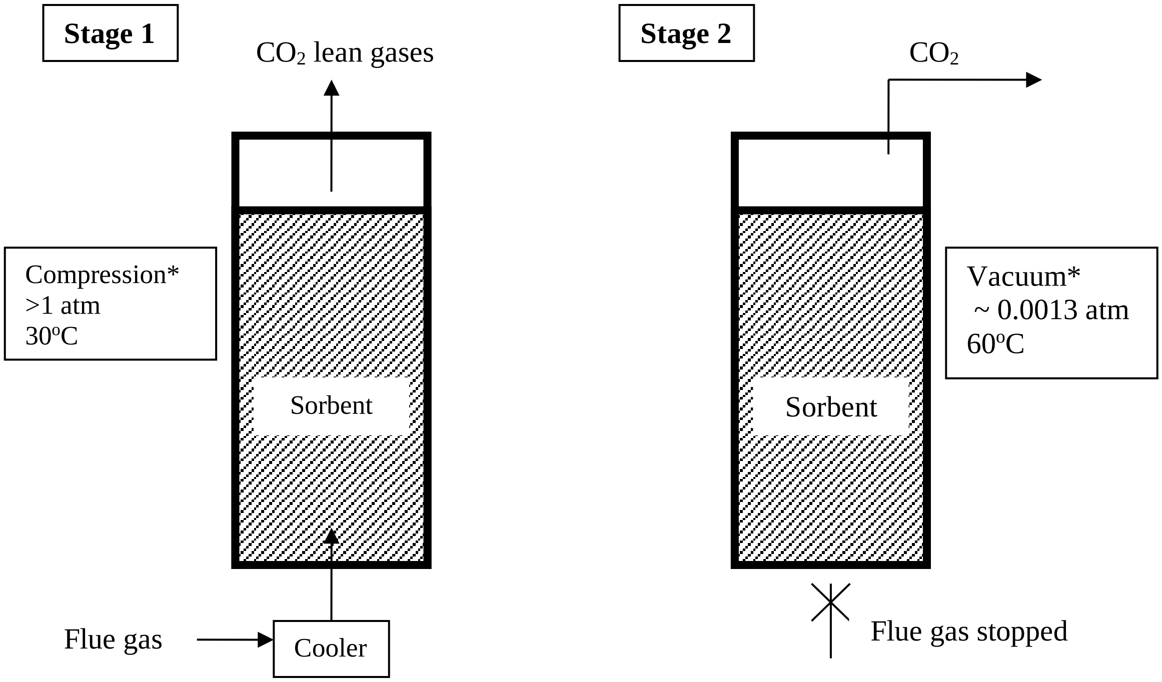


Figure 2 - Single chamber adsorption system[11].
* Pressure and temperature conditions vary with adsorbents used.

Figure 3 shows a pressure swing adsorber where two chambers pass the pressure back and forth in a continuous cycle. Flue gases are sent into one of the two chambers and pressure is applied, causing adsorption of the CO_2. The pressure is then transferred to the other chamber where a new volume of waste gas has been introduced. As that chamber is pressurized, the first chamber is depressurized and the CO_2 is collected. The cycle then continues in a switching mode as waste gases are sequentially injected into the two chambers. The connecting lines and valves shown beneath the tanks in Figure 3 control the flow of the CO_2 to one collection site and the flow of the rest of the flue gases to the other[15]. The conditions shown below in both flow diagrams apply only for one sorbent, carbon fiber composite molecular sieve (CFCMS).

Sorbent HSC⁺

The conditions for a sorbent called HSC^+ are adsorption at .0059 atm (partial pressure of CO_2) and 25°C and desorption at 0.0013 atm (partial pressure of CO_2) and 40°C. HSC^+ is used to remove CO_2 in space shuttles. Different sorbents are optimized under different conditions, but they can often be used close to atmospheric pressure and room temperature for adsorption, and vacuum combined with higher temperature for desorption[16].

Adsorption has the advantage of easily attainable conditions for proper function and regenerability; HSC^+ operates on a pCO_2 range of 0.0046 atm and 15°C while CFCMS operates at or below room temperature and atmospheric pressure conditions for both stages of the process. A relatively small amount of energy is therefore required for operation, keeping operating costs down. In addition to lower operating costs, the small range of conditions require less complicated equipment[16].

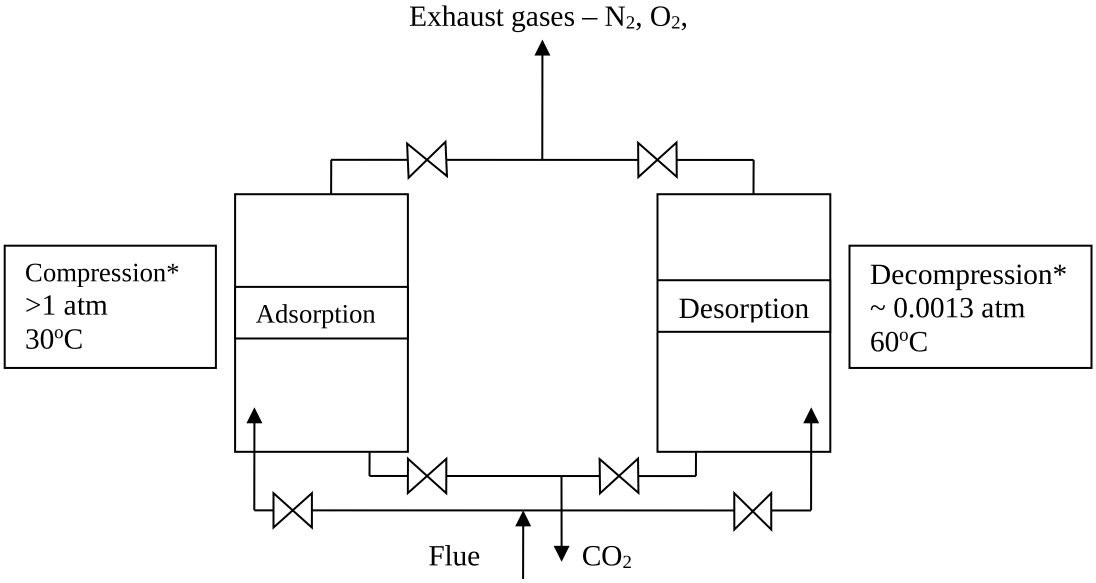


Figure 3 - Two-chamber pressure adsorption system (PSA)[15].
*Pressure and temperature conditions vary with adsorbents used.

Advantages and Disadvantages for Adsorption

Unlike cryogenic separation equipment that must withstand significant temperature changes, or liquid absorption where the solvent can form corrosive solutions with flue gases, physical adsorption only requires vessels capable of withstanding small pressure changes. PSA, like chemical absorption, is based on regenerability of the sorbent. As shown in Figures 2 and 3, the sorbent can be reused many times for CO_2 separation[12-14,16]. The energy cost for adsorption is \$6.94/ton CO_2 removed at CO_2 concentrations of 28-34 mole %. Mole percent is the same as volume percent provided that the conditions are not too extreme, such as 0°C and 10 atm (conditions should be reasonably close to ambient conditions). The cost is approximately four times greater when the mole % is from 10-11.5 (this being the most common range of CO_2 partial pressure)[7].

There are two significant drawbacks that make adsorption currently unfavorable as a stand-alone process. The first is that the system cannot easily handle large concentrations of CO_2, usually between 0.04% and 1.5%[5]. Most power plants have much higher concentrations of CO_2 in flue gases, approximately 15%[11]. The second is that available sorbents are not selective enough for CO_2 separation from flue gases. The sorbents' ability is usually based on pore size. When CO_2 is the target to be selectively adsorbed, gases smaller than CO_2 can also penetrate the pores. N_2 is the gas that most commonly fills up pore space in sorbents. This makes the process less efficient as a lower degree of CO_2 separation can be achieved in each cycle. The purity of the CO_2 stream is affected by the sorbent used, since various sorbents will adsorb varying amounts of N_2 (the most common impurity). Research to develop sorbents capable of very selectively binding CO_2 is underway. Another drawback is that adsorption is slow. For example, the HSC^+ system cleans enough air to support a full crew of astronauts in the space shuttle (only 7 kg/day[16]). While this is an acceptable rate for such a small-scale application, the cost of making this system large enough to accommodate a typical power plant would be prohibitively high. For typical materials, the residence time for maximum adsorption depends on the sorbent, but 20 min is a reasonable estimate[16]. When dealing with large volumes of flue gas, as in a power plant, this is just too slow to be practical. A list of example materials, conditions, and costs is shown in Table 2.

Despite these disadvantages, physical adsorption can play a satisfactory role in a hybrid system. Since it requires a low concentration of CO_2 for optimum performance, it could be placed after another separation process. Research is currently being conducted to find more selective sorbents, sorbents with higher capacities, better operating conditions, and more efficient packing structures. If these goals can be met, adsorption can be made a viable method for separating CO_2 in the future.

Table 2. Materials and Conditions Used in CO_2 Adsorption Processes.

Sorbent	Adsorption Temp (°C)	Adsorption Pressure (atm)	Desorption Temp (°C)	Desorption Pressure (atm)	Cost (\$/ton CO_2
CFCMS	30	1.97	60	0.001	27.8
HSC^+	25	0.04	40	0.008	Not reported
Zeolites	None reported	None reported	None reported	None reported	Not reported

Cryogenic Distillation

Cryogenic separation relies on the assumption that all components of the flue gas are removed except for the N_2 and CO_2 prior to cooling. Once all of the other gases and particulates are completely removed, the remaining gas is sent into a cryogenic chamber where the temperature and pressure are manipulated to cause the CO_2 to liquefy.

Under the right conditions (the triple point for CO_2 is -56.6^{o}C and ~7.4 atm[17]), CO_2 will condense while N_2 remains as a gas. This distillation allows N_2 to escape through an outlet at the top of the chamber while the highly concentrated liquid CO_2 can be collected at the bottom of the chamber[15].

A similar method termed "refrigeration under pressure" also condenses the CO_2 from a mixture with N_2, but uses more intense pressurization and somewhat higher temperature than cryogenic distillation. The refrigeration under pressure system is also slightly more complicated in its various components as well[17]. Following are basic flow diagrams of cryogenic distillation chambers and a refrigeration system under pressure.

Figure 4 shows a simple distillation tower. The whole apparatus is kept in a cold room. Flue gases, after having NO_x, SO_x, and H_2O removed, enter the compressor. The flow then proceeds through the heat exchanger, where the N_2 exiting the tower picks up heat from the entering flow. The CO_2 liquefies or solidifies in the tower[15].

An alternative cryogenic distillation process outlined in Figure 5 incorporates a step that separates the CO_2 from a flow that has not been pretreated (no components of the flue gas have been removed). After leaving the boiler, the flue gas enters a chamber cooled by a refrigerant stream. Water is condensed to avoid chemical corrosion, particulate matter is removed by appropriate traps, and heat is recovered. Maximum recovery of acid rain-causing gases can be effected with minimal energy penalty. CO_2, O_2, and N_2 are then directed through an adjacent chamber counter in flow to the entering gases. This helps in cooling the gases for separation. Some of the resulting gases (mostly O_2) are recycled through the boiler while the high purity liquid CO_2 is stored[18].

The method of refrigeration under pressure is shown in Figure 6. Raw flue gas enters condensers A and B to have nearly all remaining water removed. After compression in chamber C, gases enter cooling area D and split into two flows; one flow is directed through the bottom coolers (similar to A and B) and the other is passed through the heat exchanger to give heat to the exiting flow. Both entering flows are cooled prior to entering the separation unit E. The gas is then cooled further and the CO_2 is separated (as a liquid or solid, depending on conditions). The CO_2-lean (any SO_x or NO_x, N_2, O_2, etc) gas is then directed to the heat exchanger to cool entering gases before they move to the decompression turbine F. The clean gases are then released[17].

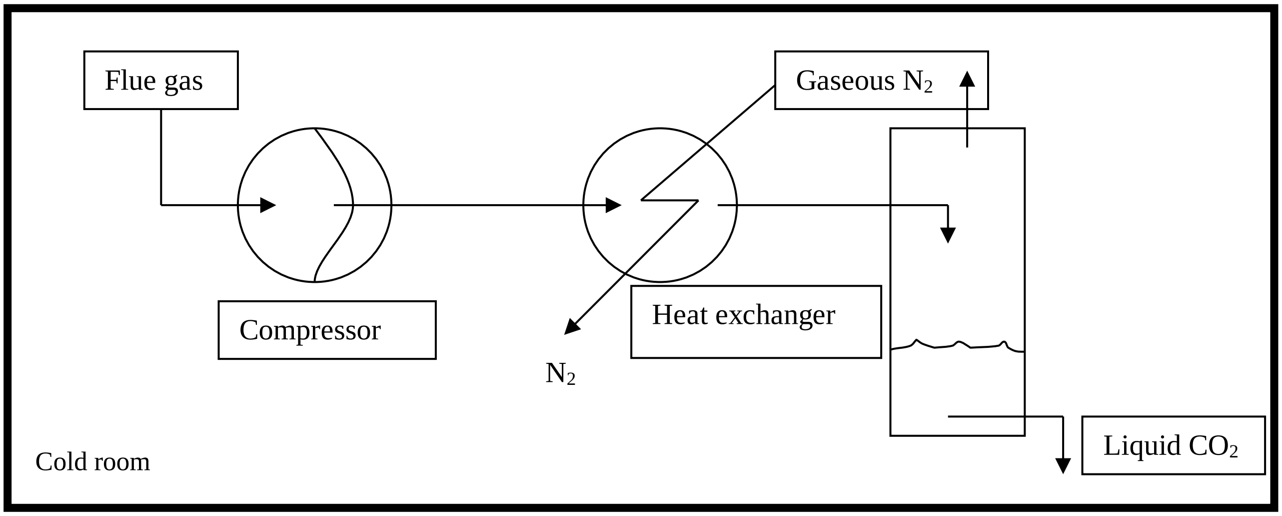


Figure 4 - Cryogenic separation (after removal of SO_x, NO_x, H_2O, etc)[15].

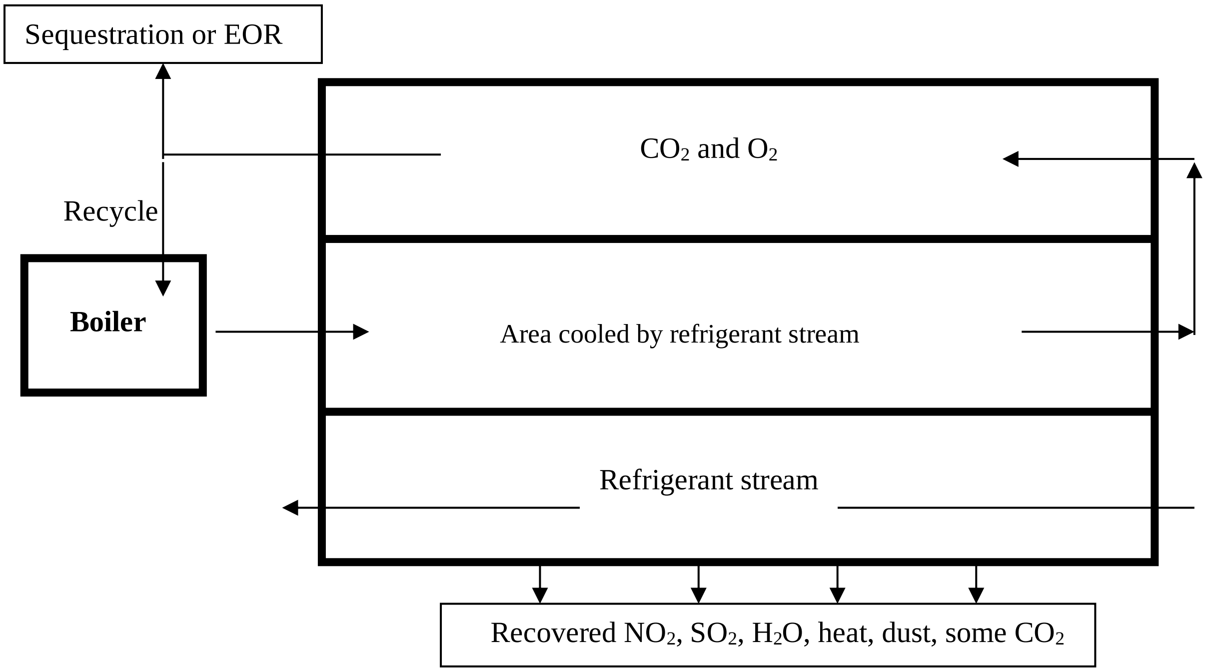


Figure 5 - Cryogenic distillation method[18].

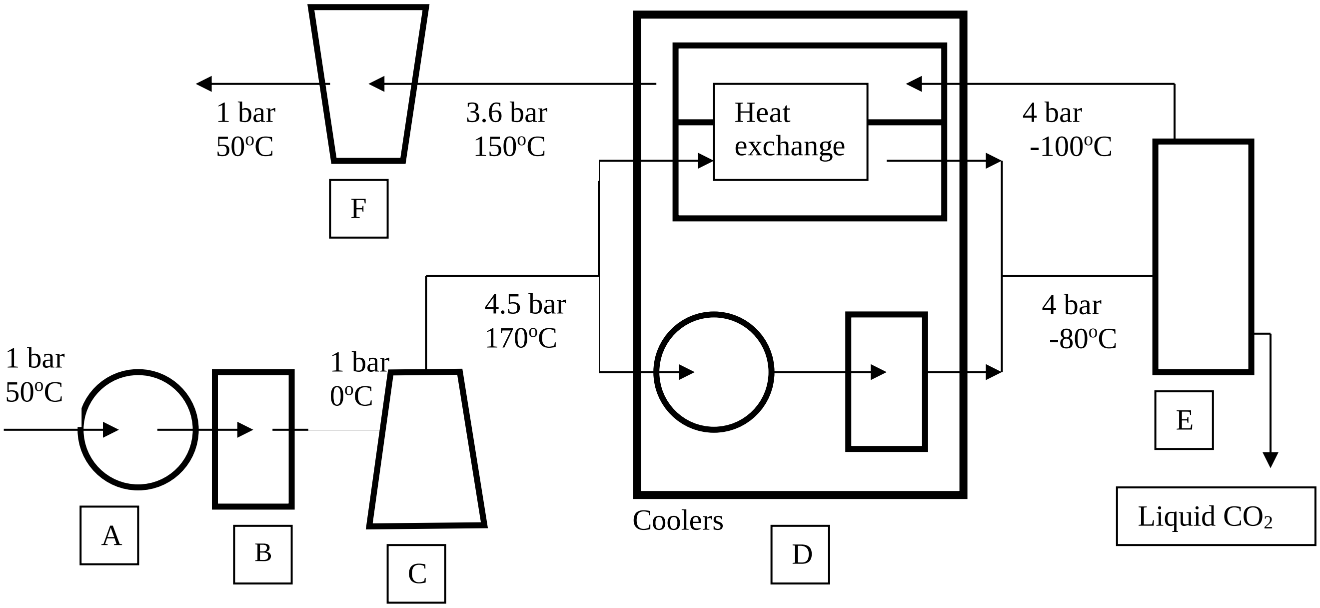


Figure 6 - Refrigeration under pressure[17].

Advantages and Disadvantages of Cryogenic Distillation

Cryogenic distillation has one advantage over most other separation processes: its product is liquid CO_2, which is ready for transport via pipeline or tanker for sequestration. In addition to being ready for transport, the CO_2 recovery is very high (CO_2 purity after distillation can exceed 99.95%)[18]. The cryogenic process, however, is extremely energy intensive. The energy required to keep the system cool (often using liquid nitrogen) makes the current process cost ineffective. The other "drawback" to the cryogenic process is that it cannot be used alone. NO_x, SO_x, H_2O, and O_2 must all be removed from the flue gas prior to the process shown above in Figure 4. If H_2O is in the stream when the gases enter the chamber, it will freeze and could clog the pipes (the water could also corrode the equipment). The cost for cryogenic distillation is predicted by lab-scale experiments to be approximately \$32.7/ton CO_2 separated[7]. This can be compared to the absorption cost of \$13.9/ton CO_2 removed and adsorption's \$27.8/ton CO_2 (as stated above).

Refrigeration under pressure offers similar benefits to cryogenic separation, with similar drawbacks. While the cost for cooling under pressure is lower than that for cryogenic separation, more energy is required to pressurize the gases. To reduce the cost, a heat exchanger may be introduced to assist in cooling entering gases and heating exiting gases. The exiting gases also power a turbine that generates energy, offering some repayment for the energy required for the rest of the process. The energy penalty for this process depends on the degree of separation. If 90% of the CO_2 is captured, the overall efficiency of the plant is decreased from 38% (before any CO_2 removal) to 26%; the efficiency is 31% when 50% of the CO_2 is removed[17]. The efficiency of 38% was an arbitrary decision by the investigators of the referenced work.

Both of these methods of separating CO_2 are fairly new and have room for improvement and optimization before their applications. They operate with similar principles, and due to their nature, are readily used in hybrid systems. Lowering the energy required and eliminating the limitations of both methods is the focus of current research.

Membrane Diffusion

The use of membranes has been established as a means of separating CO_2 from light hydrocarbons in the fuel and chemical industries. Membranes are also traditionally used to separate hydrogen gas from various other gases[5]. Inorganic, metallic, polymeric, and liquid (liquid is not very common) are all forms of membranes used today[19].

The selectivity of polymeric membranes is based on their ability to interact with the target molecule. Whatever molecule is to be separated interacts with the membrane and is allowed to diffuse across, either by solution-diffusion or absorption-diffusion mechanisms.

The principle of ceramic and metallic membranes, which are porous, is that only gases of a certain size are able to pass through the pores of the membrane. So these membranes act as a sieve to separate CO_2 from larger gas molecules. The flue gases from a fossil fuel power plant are sent at atmospheric pressure into a chamber that is divided by a membrane; the CO_2 passes through the membrane into another part of the chamber where it is collected at a lower pressure (typically 10% of the feed pressure).

In addition to the above stated membranes, gas absorption membranes are also being researched. These consist of microporous solid membranes impregnated with a liquid absorbent. In this arrangement, CO_2 selectively diffuses across the membrane and is captured and removed by the liquid absorbent. This allows for individual control of gas and liquid flows and minimizes complications such as flooding, channeling, and foaming[12]. Research shows that the thickness of the membrane plays an integral role in the permeance of the system. A membrane that is 10 μm thick would be 20 times more permeable than a membrane that is 200 μm thick[20]. The gas absorption membrane system is a hybrid of solid membranes and liquid absorption.

In Figure 7, the flue gases simply enter the separation tank and the CO_2 diffuses across the membrane. The pressure on the permiate side is approximately 10% of the feed side; this pressure difference, once initiated by a vacuum, will continually pull CO_2 across the membrane. The separated CO_2 is blown to a collection tank and the flue gases exit for further treatment, such as oxidation of NO_x and SO_x, recycling of O_2 for combustion, and condensation of water vapor. Sometimes these gases are separated prior to entering the separation tank because they can harm the membrane. If this is the case, the membrane just has to separate CO_2 from N_2[15].

With a two-stage separator, see Figure 8, the same process applies, except the gases that permeated the membrane in the first chamber are again separated in a second separation tank. This approach provides greater separation and a gas stream that is more suitable for carbon sequestration. The unpermeated gases from both tanks are sent to the same receiver for further treatment. While double separation yields a much higher purity stream of CO_2 (89.1% instead of 46.4% at 25°C with a single stage) [21], it generally costs twice as much as traditional amine separation processes[22].

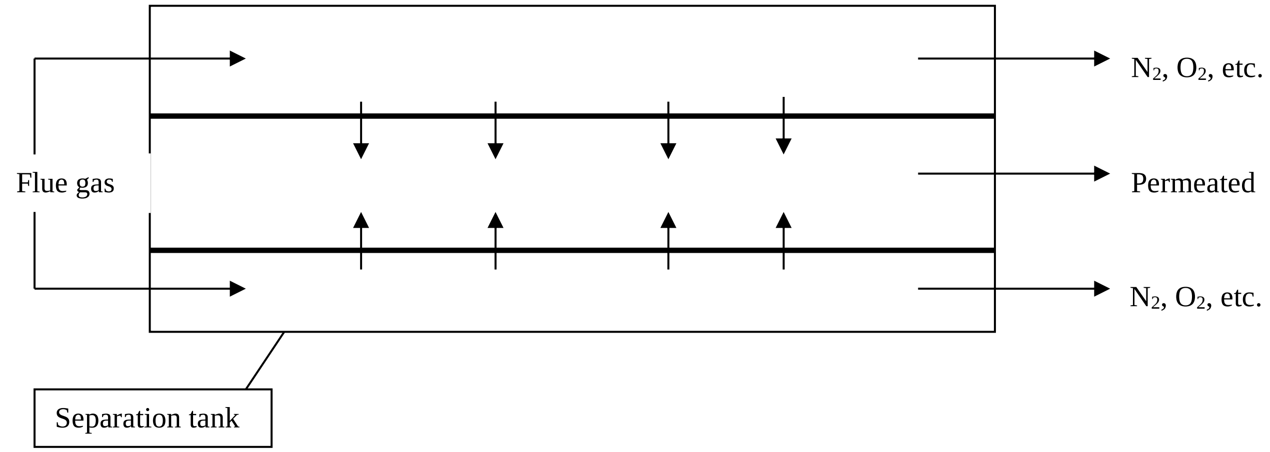


Figure 7 - Simple membrane separation chamber[15].

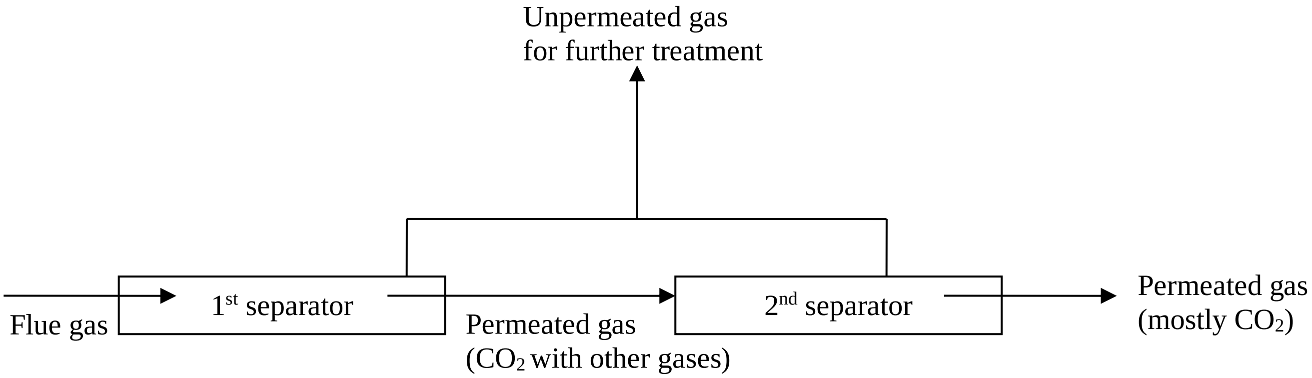


Figure 8 - Example of two-stage separator[20].

Advantages and Disadvantages for Membrane Diffusion

The greatest asset to membrane separation is simplicity. While pressure swing adsorption (PSA) requires the equipment for swinging pressure and cryogenic distillation must endure extreme temperatures, the only equipment necessary for the actual membrane separation is the membrane and fans. There are almost no moving parts and the construction is fairly simple. The flue gases must be compressed somewhat before separation (pressure is ideally approximately 1.01 atm) but this compression is much smaller than that necessary for PSA. Membrane separators do suffer, however, because they are either not selective enough or they are not very permeable to CO_2. Currently, it is a trade-off; membranes that are very selective are not very permeable while permeable membranes allow other gases besides CO_2 to permeate, requiring a secondary separation. This results in a low-purity stream of CO_2 (the exact percent was not reported in the available literature). The presence of impurities, however, should not appreciably affect the sequestration capacity of an underground formation; this is addressed in the Geosequestration section. Also, many organic membranes do not perform well at high temperatures, typical of flue gases exiting the stack. The difference between the pressure of the flue gases and the permeated gases (a factor of 10) also causes problems for membranes that are not structurally stable.

Gas absorption membranes suffer the same drawbacks that absorption does: the incoming gases can contain chemicals that foul or otherwise poison the solvents[12]. Gas absorption membranes are also less structurally stable than metal or ceramic membranes are predicted to be. A list of membranes and their conditions is shown in Table 3.

Research is being done to find new metallic, ceramic, and alumina membranes. These membranes would better withstand the high temperature of the entering gases (350°C ideally[23]) and the pressure changes associated with the gas flow through the chamber. Since gas absorption has higher permeability and selectivity for CO_2, methods of making the solvent stage of the membrane more chemically stable are being intensely researched[11,18,19]. The presence of water vapor in the pores of membranes has also been studied. It was found that when water vapor clogs micropores, permeability decreases for both N_2 and CO_2; however, the decrease to N_2 permeability was so great that it was immeasurable while CO_2 permeability decreased by only a factor of 10 (small compared to the decrease in N_2)[24]. Additionally, the membranes in development must be able to withstand the presence of SO_x and other compounds that typically pose problems for CO_2 separation units since they are located before the FGD unit.

Creation of more stable solid and liquid membranes will determine whether membrane separation can stand alone as a CO_2 capture process or whether it may have to be part of a hybrid separation system.

Table 3. Materials and Conditions for Membrane Diffusion Separation of CO_2

Material	Temperature (°C)	Pressure (atm)
Organic	25	1.01
DAMA*	25	1.00
Ideal metallic or ceramic	350	1.00

*DAMA is 2-(N, N-dimethyl)aminoethyl methacrylate (DAMA) grafted onto microporous polyethylene (PE). All materials are shown in Table 4.

Hydrate Formation and Dissociation

One method for separating CO_2 from flue gases is to use hydrate formation separation. Hydrates are ice-like structures in which water forms a cage with cavities where small gases such as CO_2 can be trapped. While other gases can get trapped in these cavities, CO_2 is often the most likely occupant. A maximum of 8 CO_2 molecules can be trapped in a cage of 46 water molecules. This gives a mole fraction of 0.148, but a weight fraction of 0.31 $gCO_2/g\ H_2O$[25]. The SIMTECHE process for hydrate separation is shown in Figure 9.

Since water readily forms hydrates with CO_2 (T = 0°C, P = 12.3 atm) the separator can capture CO_2 and allow the waste gases to escape. The flue gases enter the hydrate slurry reactor so that the CO_2 can be hydrated. Hydrates do not form above 10°C or much below

4 atm. Conditions on the ocean seafloor where CO_2 hydrates are being researched for sequestration are approximately 4°C and 8.88 MPa[26]. In the case of syngas separation (Figure 9), the CO_2 hydrate slurry goes to the slurry separator where the H_2 is removed. This is a highly pure stream and can be used for future hydrogen cells or chemical reactions. The process described above would most likely be used in an integrated gasification combined cycle (IGCC) application, but a similar process could be adapted for a hydrate separator at a pulverized coal plant. Using heat from the ammonia cooling exchangers, the hydrates are melted and the CO_2 rich stream is collected for sequestration or utilization. The nucleated water is then recycled[27].

The advantage to using hydrate formation for separating CO_2 from flue gas or syngas in an IGCC reactor is that it may not be more energy-intensive than traditional means (chemical absorption, PSA, etc) and the product can be easier for transport than CO_2 gas. Conventional amine scrubbers, pressure swing adsorption (PSA), and other methods impose energy penalties up to 35% for coal-fired plants. Hydrate formation, while not actually performed in a plant, is believed to impose an energy penalty of only 4.4% in an IGCC system[25]. In addition, the presence of H_2S actually makes CO_2 hydrate formation easier to achieve; when H_2S is 10% of the gas stream, CO_2 forms hydrates at 88.8 atm. This makes the possibility of incorporating hydrate formation separation in the near future more feasible[28].

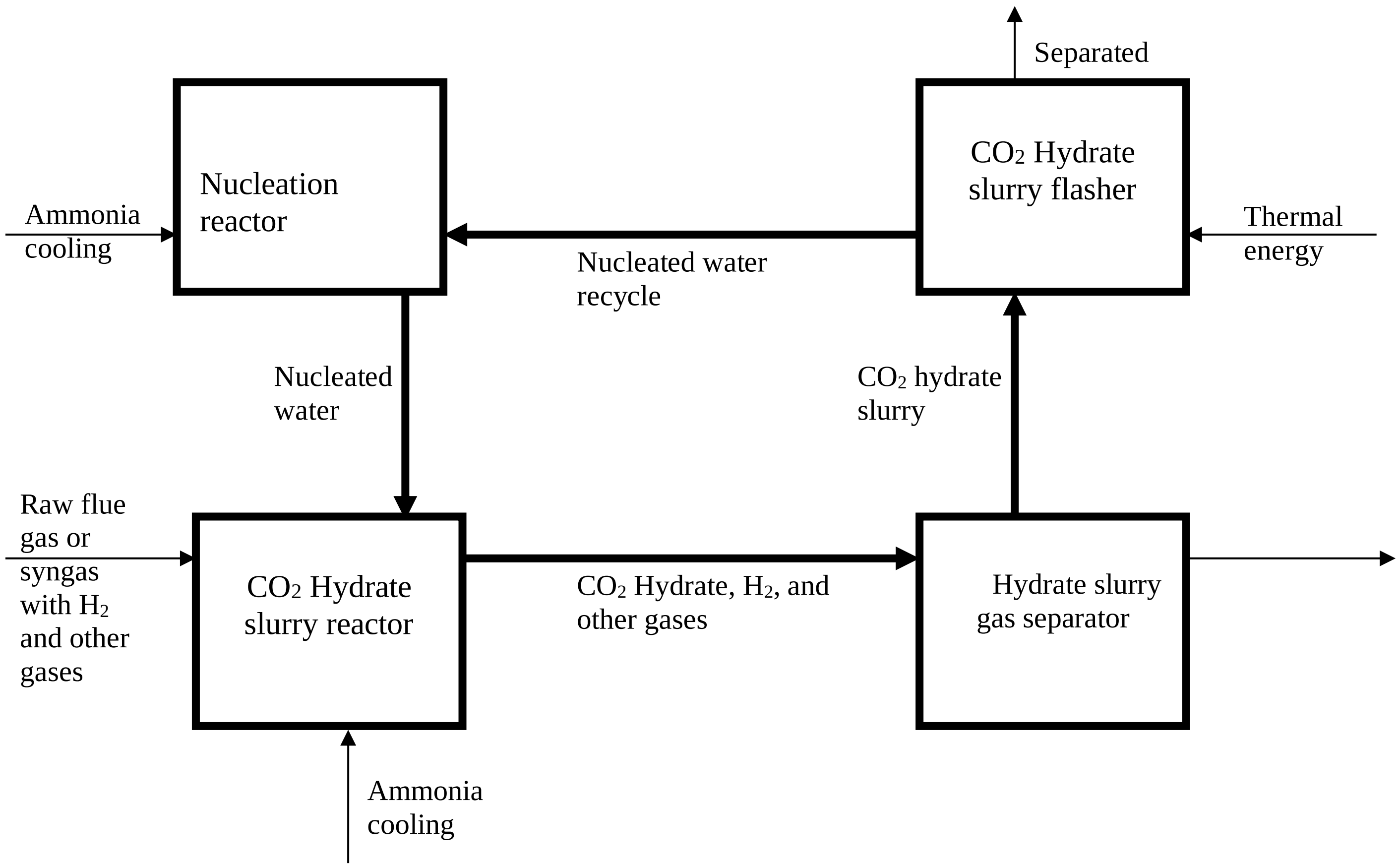


Figure 9 - CO_2 hydrate separation method for IGCC[21].

Hydrate formation is limited for current separation applications because it requires high pressures (~88.8 atm). While PSA requires high pressure, it is not of the same order as that for hydrate formation. In addition, the temperature for formation is quite low, ~32^{o}F, especially compared to the temperature of flue gases from coal plants. A significant amount of energy would be required to cool the flue gases to a suitable temperature, and then more energy would be required for pressurization.

Another concern is also the reason that hydrate research ever began. When transporting natural gas through cold areas under pressure, hydrates formed and plugged the lines. In bench-scale tests, hydrates plugged the apparatus. Mechanisms to prevent hydrate plugging must be set in place for this method to function properly in a plant application. While some conversion rates were as high as 35% (that is, 35% of the CO_2 that entered the reactor was captured in the hydrate form), better phase contacting could increase the efficiency of hydrate separation. Other major areas of improvement are how to remove the heat of formation and how to keep a steady flow despite multiple phases (liquid CO_2, hydrate, liquid water, and ice)[27].

Addition of Tetrahydrofuran (THF) for Hydrate Formation

Investigations were also performed for CO_2 hydrates that sought to maximize the formation amount. One barrier to the use of hydrate formation is the high pressure involved. It was found that the addition of THF lowered the pressure necessary for hydrate formation from 82.4 atm to 4.69 atm. In addition, it was found that lowering the temperature in presence of THF by only 6 K increased the mol % of CO_2 in hydrate form from 39% to 61%. THF is used only in small quantities and conditions are not such that THF loss or degradation should be a problem. The THF can also easily be recycled with the nucleated water after CO_2 has been liberated (see Figure9). The optimum conditions determined in this experiment were approximately 2^{o}C and 3.95 atm, 70 mol % CO_2 + 30 mol % N_2 gas mixture, and 3 mol % THF (3% when THF is added to the CO_2/N_2 mixture). Further research is being conducted to determine the effect of varying concentrations of THF and other hydrate promoters[29].

Electrical Desorption

Various methods using electricity for separating CO_2 have been proposed. One method uses an electric current to liberate CO_2 from a physical sorbent. The only sorbent mentioned in the literature found was a quinone carrier. Similar to PSA or TSA, electricity is the means to liberate the CO_2 trapped in the sorbent. The sorbent used is electrically conductive, and only a small amount (actual amount not specified[14]) of energy is required, making this a promising technology. The material proposed for this process was included in this report[14]. Very little research has been done regarding this method to date.

Redox Technology

Another method proposed by the National Renewable Energy Laboratory is to use a redox active carrier to bind the CO_2 to itself at high pressure and then release it at low pressure. The carrier's ability to bind with the CO_2 is determined by whether the carrier is reduced or oxidized; reduction allows the carrier to pick up CO_2 while oxidation causes it to release the CO_2. This cycle is shown in Figure 10. CO_2 from the atmosphere can also be separated using this process.

Gas is sent into a chamber where the electrically activated sorbent is located. At low pressure, the sorbent is oxidized so that it can bond with the CO_2 (oxidation takes place via an electrical circuit). The other waste gases are then evacuated. The pressure is raised and the sorbent releases the CO_2. Once the CO_2 is released, the sorbent is reduced, again via the circuit, so that it can pick up more CO_2 in a new cycle[30].

Electrochemical separation is a relatively new process, but it has promise, especially when used to liberate CO_2 adsorbed onto certain materials. No cost data were included in the results from preliminary testing (probably because it hasn't reached bench-scale testing yet). If coupled with a clean energy source, high separation rates for very low energy input can be achieved.

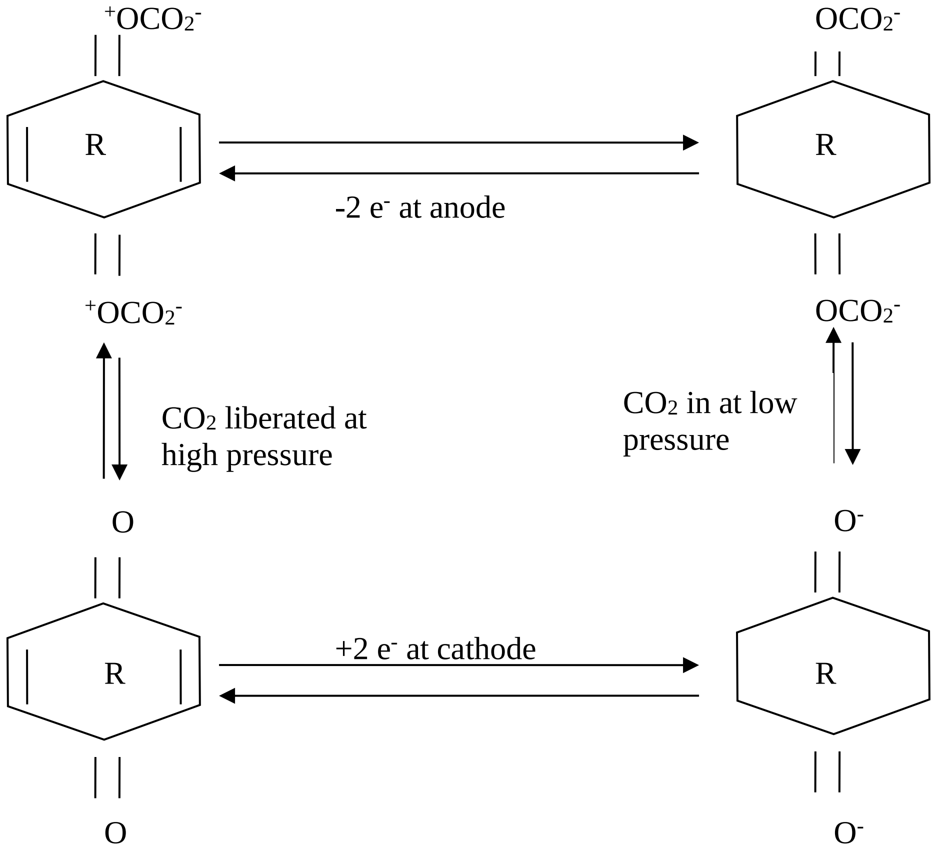


Figure 10 – Redox cycle for quinone carrier[30].

Ammonium Carbonation

Separation of CO_2 from flue gas streams can be achieved by reacting the CO_2 with ammonia gas and water vapor in a gas-phase reaction. The reaction proceeds according to the following equation:

$$CO_2 + NH_3 + H_2O \rightarrow NH_4HCO_3\ (s)$$

This reaction can be achieved by bubbling raw flue gas through an aqueous ammonia solution. The NH_4HCO_3 forms a stable solid while the N_2 and other gases that were in the flue gas stream continue through for release or treatment. In testing[11], the flue gas was bubbled through a water bath kept at 40°C and then sent to the reactor to be bubbled through the ammonia solution. In bench-scale testing[12], the reaction proceeded at room temperature and ambient pressure, indicating that the energy penalty for this method would be lower than most current methods (such as amine scrubbing, adsorption, etc.). It should be noted here that the solid product is to be used as a soil fertilizer, instead of being regenerated to recover the CO_2. Maximum CO_2 removal percentages were reached after approximately 400 min of residence time. The flow rate ratio (NH_3:flue gas) that yielded the highest CO_2 conversion percentage of 48% was 0.12; lower flow rate ratios yielded lower conversion rates. While a higher NH_3:flue gas ratio yields a higher conversion rate, computer modeling suggests that 20-60% conversion would be the best return. Another promising result of this study[12] is that the residence time in the reactor can be cut from 188 s to 47 s if the flow rate of the gas mixture is quadrupled (these times correspond to the 20-60% conversion, which takes less time than the 100% conversion). Decreasing residence time had no measurable effect on the conversion rate. This shows that if a large-scale version of this apparatus is used, large volumes of flue gas can be efficiently cleaned. This process also removes SO_2. The efficiency of SO_2 removal reaches its maximum after 0.4 s, so it too is a very fast reaction[9].

Another aspect taken into consideration was surface area of the reactor. When the reaction was taking place, it was observed that the ammonium bicarbonate formed on the walls. A vacant reactor and one packed with glass wool were tested for CO_2 removal efficiency. The reaction rate was the same for both cases, indicating that the reaction proceeds in the gas phase independent of reactor surface area[10]. This process is shown in Figure 11.

In addition to being fast (see above) and efficient, this process yields a valuable product – fertilizer. China has used a similar process for 40 years to currently produce 28.7 million tons of ammonium bicarbonate per year[31]. Selling the fertilizer would help offset the cost of the process and would aid in soil and subsoil sequestration of the CO_2. The fertilizer would be used by plants in photosynthesis, fixing the CO_2. The fertilizer would also facilitate plant growth, a means of separating CO_2 from the atmosphere and sequestering it. Further studies to ascertain the reaction kinetics and optimal reactor conditions could show this to be a viable process for CO_2 separation[10].

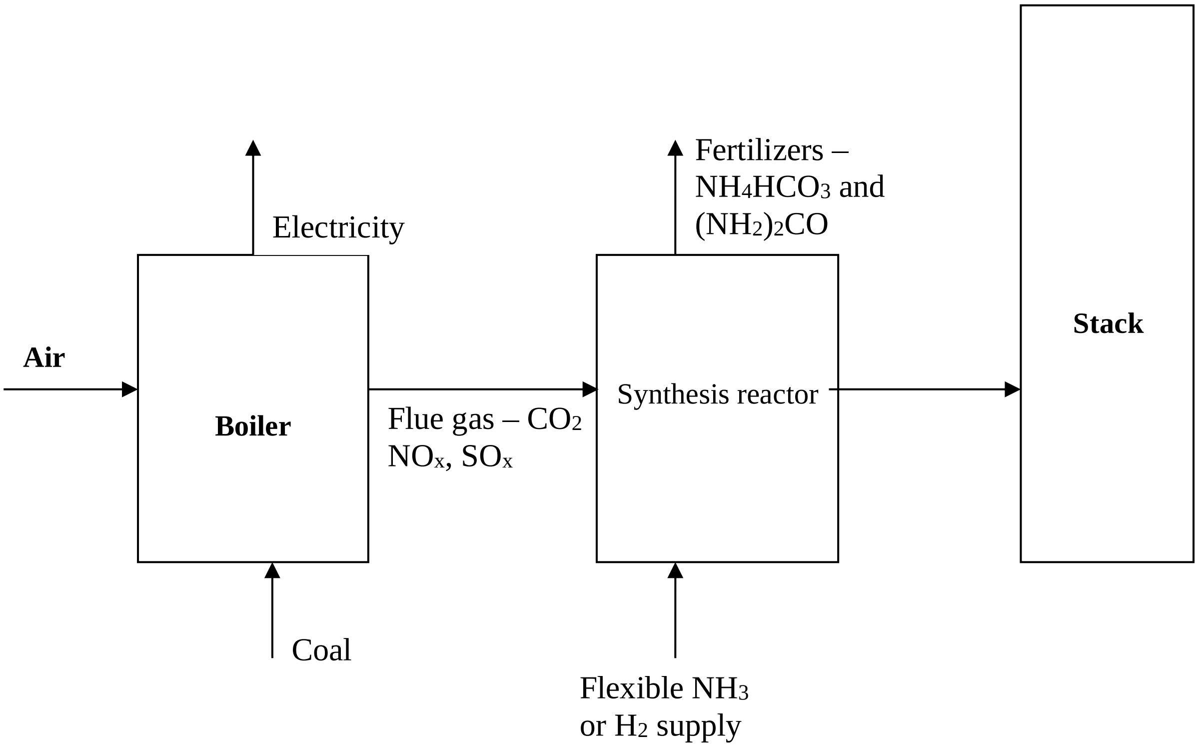


Figure 11 – Ammonium Carbonation to Produce Valuable Fertilizer.

Table 4. Materials and Conditions for CO_2 Separation by Absorption, Adsorption, and Membrane Diffusion

Process	Material	Temperature (°C)	Pressure (atm)	Operating Cost ($/ton CO_2)
Absorption	*Liquid*			
	MEA	50 (A) & 120 (R)	2.24 (A) & 1 (R)	13.9
	MEA (with Fe)	55 (A) & 120 (R)	1 (A) & 1 (R)	NR
	PSR	50 (A) & 100 (R)	2.24 (A) & 1 (R)	NR
	K_2CO_3	45 (A) & 55 (R)	1 (A) & 0.15 (R)	NR
	Solid	800 (A) & 1000 (R)	Atmospheric	NR
	LiOH			NR
Adsorption	CFCMS	30 (A) & 60 (D)	19.7 (A) & 1 (D)	27.8
	HSC^+	25 (A) & 40 (D)	0.039 (A) & 0.008 (D)	NR
				NR
Cryogenic		-56.6	7.4	32.7
	Refrigeration under pressure	-100	3000	NR
Membranes	Organic	25	1.01	NR
	DAMA	25	1.00	NR
	Ceramic, metallic (ideal)	350	1.00	NR
Hydrate		0	12.3	NR

A represents absorption or adsorption
R represents regeneration
D represents desorption
NR = not reported in the literature
Moisture content and particulate amounts (such as mass) were not found in the literature for any of the above processes.

All costs reported in Table 4 are operating costs only; replenishing solvent for absorption, cleaning sorbent for adsorption, and other maintenance costs are not included. Capital cost for purchase and installation of separation units is not included either. The cost for membrane separation is ~0 because the process proceeds by diffusion. Some small energy penalty will be entailed from fans used to move the flue gases, but this was not reported in the literature.

Summary of Development Status

Absorption using chemical solvents is already in commercial application. The solvents currently used are not as efficient as the next generation being developed. These new solvents are in the pilot plant testing stage. Physical adsorption is used in some chemical commercial applications, but not for CO_2 separation. Development of a sorbent that can function despite high CO_2 concentration and is selective enough to be economically viable is still in lab testing. Cryogenic distillation is also used in industry to produce pure CO_2, but not in the quantities involved in flue gas separations. Air separation units also operate by cryogenic distillation. The energy requirements and other costs associated with this method inhibit progress. Cryogenic distillation for CO_2 separation is still at the bench testing phase. Membrane diffusion is also used in some chemical applications, but not for CO_2 separation yet. Development of membranes capable of surviving and functioning well at pre-FGD conditions is necessary before testing can get out of the lab test phase. In all of the above processes, trace constituents of the flue gas are emitted to the atmosphere or treated further in some other process. The literature reviewed for this summary only addressed CO_2 separation, not further treatment of the flue gas. Separation by hydrate formation, electrical desorption, and ammonium carbonation are all novel concepts in laboratory testing.

Ranking of Most Promising Technologies

If all of the methods above are considered and ranked, it appears to us that the most promising individual method for CO_2 separation is membrane diffusion. The conditions are the most easily attainable since ideal pressure is atmospheric and temperature can reach up to 350^{o}C. This higher temperature allows the system to operate without a cooler since the high temperature flue gases do not damage the membrane. While polymeric membranes capable of operating under these conditions have not yet been discovered, metallic and ceramic membranes show great promise. In addition, due to the nature of the membranes, the energy required for operation is relatively small. The gas diffuses across the membrane, so the only energy penalty is that necessary to move the gas through the system. Also, membrane separation units are predicted to be easy to retrofit to existing power plants, allowing current plants to remain in operation (retrofitting is easy enough that proposals have been made to research placing small filters on car tailpipes to separate CO_2 from exhaust). The only drawback to membranes such as those described above is that they are still at the research and development stage; no material yet has been found to operate at a high enough temperature. Thus, the cost of these membranes is largely unknown. The future for membranes is very promising, however, making membranes appear to be the most promising CO_2 separation option.

The second most promising process is absorption. The conditions are relatively easy to meet for absorption and regeneration, causing the energy penalty to be fairly low. Since absorption is a well-established process, much is known about it, guiding further research and improvement. Developing new solvents that are resistant to degradation and not corrosive to the equipment is necessary. Also, easier regeneration and faster loading are issues to be resolved prior to use of absorption. Retrofitting existing plants with chemical absorbers is predicted to be relatively easy, however, especially since some coal-fired plants already have chemical absorbers incorporated in their designs**.**

Though absorption is second in our ranking, the Mitsubishi and Econamine FG processes could make absorption the preferable method for separating CO_2 if they are as efficient in application as they have been in pilot testing. The low energy requirements could make these processes as efficient as a membrane separation system for a traditional coal-fired system.

Adsorption is third as it has the next lowest energy penalty for operation. The conditions for PSA are not as difficult to manipulate or achieve as for cryogenic distillation, but are still more difficult than absorption or membrane diffusion. Finding new sorbents with better selectivity and determining the best conditions for adsorption will determine whether this process is viable for the future; current materials do not show a high enough CO_2 selectivity to make adsorption cost effective. Retrofitting existing plants with adsorbers would be more costly than absorbers and membranes because its equipment is more elaborate than the first two and adsorption is not a current separation method (unlike absorption). Large-scale separation by adsorption has not been initiated as of yet; better separation is required before this technology moves to the next stage in development.

The least promising process to us is cryogenic distillation. While it does deliver a highly pure stream of liquid CO_2 that is ready for transport and sequestration, the conditions are hard to achieve and maintain, causing the highest energy penalty. In addition, the equipment is much more elaborate than the other methods to withstand the extreme conditions necessary for proper function. Retrofitting with cryogenic distillation equipment would suffer the same drawbacks as adsorption: it is not already in use (so it would not be a mere upgrade, like absorption) and its equipment is expensive. Further research to find methods of making the conditions for distillation more easily attained will determine whether cryogenic distillation will advance to pilot-plant testing.

Hydrate formation, electrocatalysis, and ammonium bicarbonate formation are all very new concepts for CO_2 that are still in lab testing. These methods, upon further investigation, may prove efficient enough to progress to bench-scale testing in the near future.

Hybrid systems are a new concept that has reached the pilot-test stage in development. The PIEMSA plant in Spain uses cryogenic distillation to separate air components and absorption to separate H_2 from the raw syngas. These two processes do not specifically target CO_2, however, after separation, CO_2 is the only gas left, making it easy to sequester.

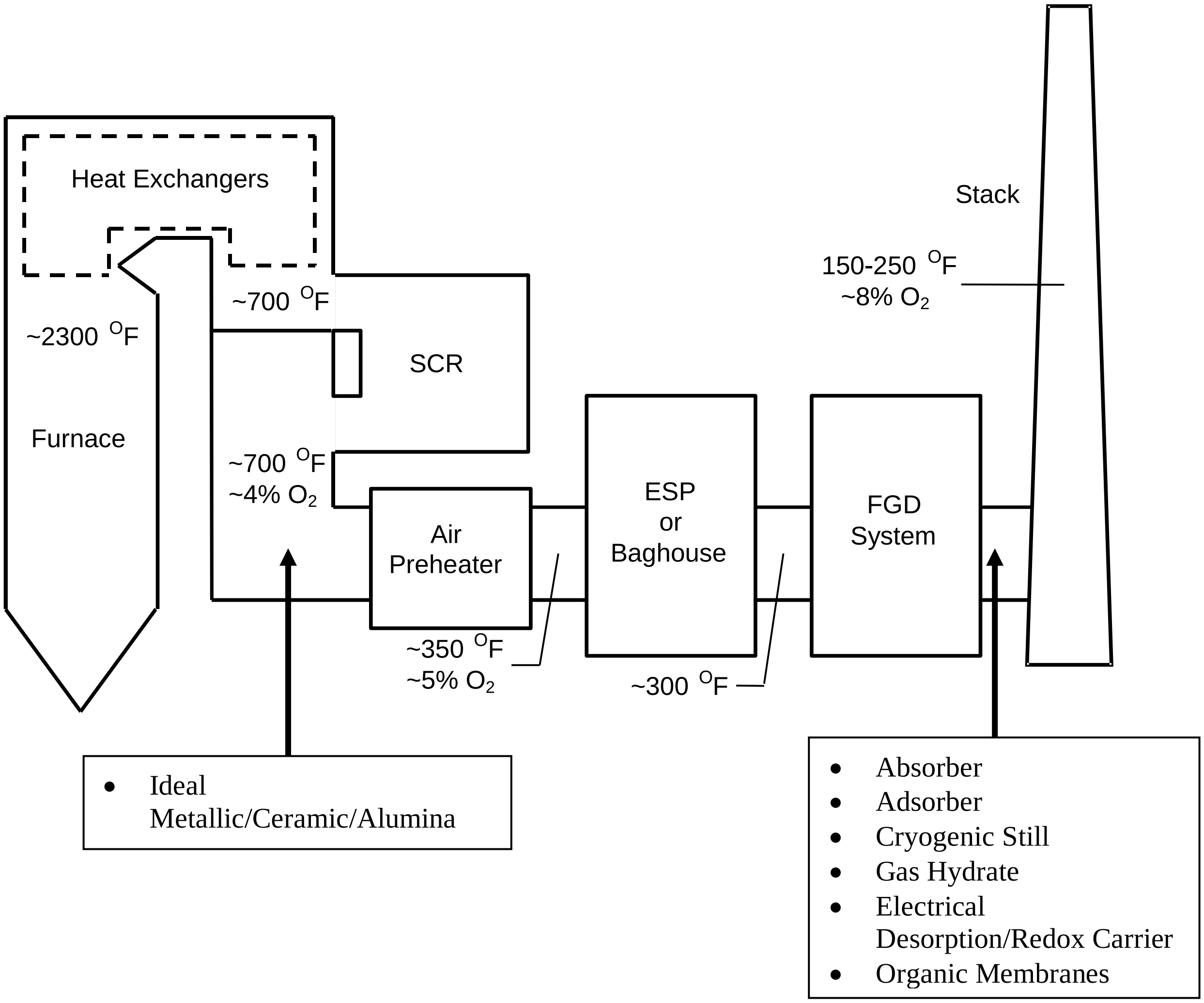
The most promising design concept for a hybrid system is IGCC (PIEMSA and the commercial plant in Sweden are examples). Other hybrid systems are possible where multiple methods are combined to offer higher degrees of CO_2 separation. These systems are not as efficient as IGCC, however, because the conditions for each separate process are very different from the rest. For example, combining chemical absorption with hydrate formation to separate CO_2 in two steps and have liquid CO_2 as the product would require a large amount of energy; there is a difference of almost 200°C between the regeneration temperature and the distillation temperature and a pressure difference of almost 6.58 atm. With further research, hybrid systems utilizing hydrate formation, ammonium bicarbonate formation, and electrocatalysis (with the four traditional methods compared above) may be the choice for power plant design due to their streamlined integration of processes, high CO_2 separation, and capability to utilize the other components of the separated gas streams.

All of the costs included above are for operation only, unless otherwise specified. Capital costs for membranes cannot be determined since satisfactory membranes have not yet been developed. Suitable materials for adsorption have also not been identified, so their cost is unknown. Absorption has relatively known capital costs, but the suppliers of the equipment and solvent determine those prices. Also, MHI and the makers of Econamine FG™ have not released prices for their processes or equipment. Finally, the cost for the equipment necessary for cryogenic separation was not found in the literature, probably because it has not reached pilot testing yet.

Selection of a Separation Technology

Based on the results of this literature review, it is reasonable to select absorption as the currently best method for CO_2 separation. A typical flow diagram showing the basic unit operations of absorption is shown in Figure 1. It is expected, however, that once membrane materials are developed to carry out the separation at relatively high temperatures, membrane separation will be the most economical approach. This is a subject of current research.

Although Figure 12 places most of the separation systems at the stack, processes such as cryogenic distillation, some absorption and adsorption, and gas hydrates will require further cooling and compression (despite stack conditions) of gas prior to operation. This will raise the cost, but the units are placed at stages that best satisfy their operating conditions.



- Ideal Metallic/Ceramic/Alumina

- Absorber
- Adsorber
- Cryogenic Still
- Gas Hydrate
- Electrical Desorption/Redox Carrier
- Organic Membranes

Figure 12 - Placement of Various Separation Systems Based on Operating Conditions.
(For conditions of each process, see Table 4).

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II. GEOLOGIC SEQUESTRATION OF CO_2

Once CO_2 has been separated from the flue gas stream emitted by a coal-fired power plant, the CO_2 must be safely and permanently stored in order to mitigate the build-up of CO_2 in the atmosphere. In areas far from the ocean, geologic sequestration is the most viable method by cost, safety, and permanence for storing CO_2. This can be done in underground saline aquifers, unmineable coal beds, or as part of enhanced oil recovery (EOR).

The exact amount of CO_2 that can be sequestered underground is highly uncertain; some estimate that only 100 Gt can be stored worldwide while others estimate that over 200 Gt can be stored in Europe alone[1]. Another estimate that 1% of all onshore basins' area can be used for CO_2 sequestration yields 320 Gt CO_2 safely stored. A global average cannot be ascertained because there is no global average reservoir. In addition, the amount of pore space in coal seams that can be occupied by injected CO_2 is also debatable. High estimates that a large fraction of pore space can accommodate CO_2 increase storage potential estimates by more than a factor of 10 over lower estimates[2]. Further research regarding how much of an aquifer or coal seam can actually be occupied by CO_2 will yield more accurate estimates of their storage capacity.

Saline Aquifers

When CO_2 is injected into a saline aquifer, carbonate ions form. These ions can react with aqueous calcium, magnesium, and ferrous iron ions to form carbonate minerals (calcium carbonate – $CaCO_3$, magnesium carbonate – Mg_2CO_3, and iron oxide – Fe_3O_4, respectively). These solid minerals then precipitate out of solution to the bottom of the aquifer. This method is promising because, once reacted, the CO_2 remains part of the mineral for geologic time periods (millions of years), never entering the atmosphere. Additionally, this process has no harmful by-products; the carbonation process is part of the natural method by which nature weathers down mountains.

In principle, most of the injected CO_2 would form carbonate minerals while the small amount remaining would exist as carbonate ions or dissolved CO_2. This retention of unreacted CO_2 may not occur in nature, however, so dealing with free CO_2 is addressed below. The carbonation process can also be performed *ex situ* in reactors where conditions can be manipulated to speed up the mineral carbonation reaction (actual rates vary, but some estimate that 1000 $mtCO_2$/hr can be sequestered, see Figure 13). The only obstacle to implementation of aquifer disposal is that it takes significant amounts of time (thousands of years, see Lackner) for the reaction to proceed at the conditions present in an underground aquifer. Therefore, sequestration in an underground aquifer relies more on CO_2 dissolution than fixation as a mineral.

Unmineable Coal Seams

Another method for sequestering CO_2 underground is to inject the CO_2 into an unmineable coal seam. Unmineable coal seams are either too deep to mine or too remote for a mining process to be economical. This approach has two benefits: the first is that the CO_2 is very strongly attracted to the coal, so it remains there for long periods of time; the second is that there is usually coal-bed methane (CBM) trapped in the pores of the coal. Since CO_2 is more strongly attracted to coal than methane, the methane is displaced by the CO_2. This methane can be captured and used as an energy source, offsetting some of the cost for separating and sequestering the CO_2. This process shows promise because it can earn back some of the cost required to sequester the CO_2. The CO_2 adsorbed by the coal can be released if seismic activity, a severe temperature increase, or a severe pressure decrease occurs. A large release of CO_2 could be disastrous; therefore extensive investigation into a site would be necessary. The criteria for coal bed sequestration are very similar to the aquifer criteria discussed below.

Selection Criteria for Underground Saline Aquifers

Safety is, of course, a primary issue for CO_2 sequestration, whether injection into a coal seam or saline aquifer is performed. A sudden large release of CO_2 (CO_2 is denser than air) could be devastating to nearby wildlife and humans. Selection of a suitable sequestration site is therefore extremely important. The integrity and viability of a sequestration site can be determined by following certain criteria for selection. The following criteria are equally important; all must be addressed and satisfied for further investigation to be worthwhile.

The first criterion is geologic condition. CO_2 should not be sequestered in areas near faults since the resulting cracks within an aquifer may allow CO_2 to escape to the surface. Sedimentary basins are large areas formed from the erosion of nearby mountains. The rocks in these basins are formed from the sediments washed down from the mountains. Nearly all rocks in the Tennessee valley are sedimentary, with only small amounts of metamorphic rock. Sedimentary basins are the areas of choice because they contain porous rocks and various energy resources (all of the coal and oil in the Tennessee valley is in these sedimentary basins), and they are mostly free of severe faults or volcanoes[3]. A concern that must be addressed when choosing a site is not only whether faults are present initially, but whether faults are likely to form due to increased pressure from the injection of CO_2.

As CO_2 is pumped into the ground, the pressure increases. This pressure can become so great that weak points in formations (not necessarily faults) break and the containment is compromised. Extensive investigation must be done at injection sites to insure that they are not only stable with regard to faults (many old, inactive faults are present in the Tennessee valley), but that the rock is strong enough to withstand the pressure increase associated with injection[4]. No information regarding specific tests to determine the stability of an aquifer was found in the literature, but various methods for measuring underground rock formations can be employed. Sonar and other imaging processes can show cracks and weak points in aquifer walls at a potential site. Induced seismic activity has been noted at many injection sites around the world. Most seismic activity registered below 1 on the Richter scale, but two instances in Colorado had seismic activity registering above 5.0. The maximum seismic level before an aquifer can be compromised depends on the aquifer’s structure. Thin-walled aquifers would easily be ruptured with low levels of seismic activity; thicker walls would make an aquifer more resistant to rupture. Geologic data and imaging can assist in determining the tolerance of a site for seismic activity.

The second selection criterion is local geothermal conditions. The pressure in a sedimentary basin increases with depth, the same as it does in the ocean, 9.87 atm for every 328 ft depth[5]. A temperature gradient of 4.28°C/328 ft is typical. It is considered ideal to sequester CO_2 in a supercritical state (at least 31.1°C and 73 atm) because it has higher density than gaseous CO_2, causing the transport properties of supercritical CO_2 to be more favorable in an underground aquifer than those for gaseous CO_2. The accepted threshold to achieve the supercritical state at injection is 2625 ft depth. This depth does vary from basin to basin, due mostly to tectonic activity, but it is a reasonable approximation for the Tennessee valley. Consideration of all temperature influences in the area is necessary to ensure proper storage; basin type, proximity to deep heat sources, basement heat flow, thermal conductivity of the sediment, and surface temperature are all parameters for consideration[3].

The third criterion is hydrodynamics. Injected CO_2 has different flow characteristics depending on the phase in which it exists. The expected phase for CO_2 during injection is a supercritical fluid. When CO_2 is dissolved in the formation water, (formation water being the water that is in the aquifer) the solution behaves much like regular formation water. This solution is slightly denser than the rest of the water, so it usually travels along the bottom of flow paths. Some aquifers have very slow formation water flow (as low as 0.01m/yr[3]), so CO_2 dissolved in the water will not travel very far during long periods of time. Most underground water flows are controlled by high elevation recharge and low elevation discharge. Because of this, CO_2 would ideally be injected deep into the ground (at a depth with conditions beyond the critical point of 31.1°C and 73 atm) at high elevations and allowed to flow with the formation water. Formation water flow modeling must be performed to ensure that the conditions along the flow path keep CO_2 in its supercritical state. Injection at a higher elevation increases the time that the CO_2 is in water (allowing more time for mineral carbonation) before the water discharges at a lower elevation. Any CO_2 that does not participate in mineral carbonation is sequestered for millions of years by hydrodynamic and physical traps, effectively never returning to the atmosphere. Physical trapping of CO_2 occurs when CO_2 remains in solution. This CO_2 will be sequestered for long periods of time because formation water flow is slow and flow paths are often quite long (in the range of kilometers). Hydrodynamic trapping is even better, since it is a form of physical trapping, but the formation water flow gets trapped in a cavity or other feature that keeps that volume of formation water from continuing on its path. This allows more time for mineralization and keeps some of the physically trapped CO_2 from flowing to the discharge area. The possibility of supercritical CO_2 being released upon formation water discharge has yet to be addressed and modeled[3,6]. If supercritical CO_2 is present at formation water discharge, the fluid would gasify and enter the atmosphere.

The fourth criterion is hydrocarbon potential and basin maturity. Due to the lack of large oil fields in East Tennessee, this is not of great concern. If a basin is found to be rich in oil, extraction of oil would be preferable and then CO_2 could be used in an enhanced oil recovery (EOR) application. This would extract more oil and sequester CO_2 at the same time. EOR has been extensively practiced in the Midwest, especially Texas. If the basin has been depleted of oil and is already saturated with CO_2 (from EOR), a more suitable site will have to be found[3].

The fifth criterion is social and political concerns. Public approval of injection (safety must be ensured), adequate transportation facilities (public acceptance of pipelines), the role of local authorities in the overall process, and land usage must be addressed. In addition, if CO_2 is transported out of the Tennessee valley via underground water flow, responsibilities and jurisdictions with neighboring authorities must be negotiated. These, of course, must be resolved for a specific site. Once these criteria are thoroughly considered regarding a site, the potential for sequestration in a basin can be determined[3].

A promising site for injection is one that satisfies the above criteria as an initial test. Once a site is found that meets the criteria, more extensive investigations can begin that include necessary measures to transport the separated CO_2 to the site. An accepted estimate of the cost for onshore sequestration in an underground aquifer is \$4.7/mtC. This cost includes a small amount of transport (pumping the CO_2), preconditioning (if necessary), and injection. No estimates for the cost of each component in this process were provided in the literature. The cost of investigating the site is not included in this estimate[1]. Preconditioning may be necessary for CO_2 injection, depending on the separation method used. For example, if absorption is used, the CO_2 exiting the regeneration column will be hot; if this gas does not cool during transport, some cooling will be necessary prior to injection.

In addition to general information regarding specific underground aquifers, other information is needed. Even with highly sophisticated and accurate geochemical computer models, flow of formation water and injected CO_2 will change as mineralization occurs. Porosity and permeability will change as CO_2-formed minerals precipitate out of solution, which could change flow characteristics in the aquifer (some paths could be blocked by precipitate accumulation). Acidic conditions caused by the injection of flue gas should, however, prevent minerals from forming near the injection point. As mineralization and dilution of the acid in the formation water neutralize the acidity, precipitation most likely will occur far away from the injection point.

Also, the rate of CO_2 injection must be matched with the water flow rate in the aquifer. The formation water flow can be measured (as estimated above to be 0.01m/yr); the rate of CO_2 injection will depend on this rate. Flows must be matched so that overpressurization does not occur. Mineralization rate must also be considered to insure proper dissolution and spreading while preventing over-pressurization (due to decreased porosity from precipitation of minerals). Further research is needed to develop more accurate models capable of predicting conditions following mineralization (further down the flow path), dissolution/precipitation reactions (preliminary research in this area suggests that dissolved CO_2 does not affect the dissolution rate for carbonated minerals), and effects of high CO_2 levels on silicate and carbonate formation[7].

Current Status

Storage in underground aquifers is already underway. Statoil, a Norwegian fossil fuel company, is sequestering 1 Mmt CO_2/yr in the Utsira formation under the North Sea. A carbon tax issued by Norway results in a higher penalty for atmospheric release than the cost for sequestering the CO_2[8]. The tax for the output of the 150MW Sleipner West power facility would equal approximately \$134,000/day if sequestration were not performed. The Natuna field in the South China Sea is currently being developed to sequester approximately 100 Mt CO_2/yr in the very near future for both commercial and research purposes[9]. These two cases will provide data regarding offshore underground sequestration.

The long-standing practice of EOR provides substantial insight into what is required to sequester CO_2 underground onshore. Data regarding tectonic activity, sediment porosity, formation water flow, pressure/temperature gradients, and other features of underground formations have all been extensively gathered for EOR applications. The task of compiling these data for a specific underground aquifer site, however, is difficult in this region; since EOR has not been performed in East Tennessee (no large oil fields for application), geologic data are either incomplete or difficult to compile[3]. Other areas in the Tennessee valley do contain oil reservoirs, though. If EOR has been used in these areas, data regarding formation water flow and other pertinent features may have been compiled. These data could be used for CO_2 injection determinations. To date, no commercial projects for onshore underground CO_2 sequestration have been initiated.

Forced Carbonation

Forced carbonation of calcium, magnesium, and ferrous iron is a related process that can be used for sequestering CO_2. In this application, an artificial environment is created that facilitates the carbonation of these metals. This environment would most likely be a large chamber designed to withstand high temperature and pressure, conditions that speed up mineral carbonation. The chemical process is the same as that which occurs in underground aquifers. The advantage to this is that it greatly speeds up the carbonation reaction. The exact amount of time required for carbonation was not found, but as shown in Figure 13, 24,000 mt CO_2 can be sequestered in 24 hrs. This ensures that CO_2 will not be released to the atmosphere (since this is an *ex situ* application, no injection occurs) and it allows more aquifer volume to be used for CO_2 injection. More free aquifer volume is the result of this operation because some CO_2 can be used for carbonation while the rest can be injected into the aquifer. As a reference, Kingston steam plant emits daily a cube of CO_2 approximately 807 ft per side. Mineral carbonation of this same volume of CO_2 would yield a cube with a side of only 8.07 ft. The two most promising minerals to be used for forced carbonation are olivine and serpentine; approximately 0.67 tons CO_2 can be sequestered by 1 ton of olivine while 0.5 tons of CO_2 can be sequestered by 1 ton of serpentine. Any leftover CO_2 following mineral carbonation would be either recycled into the reactor or injected underground. An estimated, average cost for forced carbonation is $31/ton CO_2; this cost includes all preconditioning, transportation, operation of equipment, and disposal. Capital cost and installation are not included here since this is a relatively new process that has yet to be pilot tested.

The concept here is that CO_2 from a fossil fuel power plant will be transported to a carbonation reactor where it will react with crushed olivine or serpentine. The reaction is facilitated by stirring the minerals, CO_2, and the appropriate fluxing agents in solution. Products of the reaction include magnesite ($MgCO_3$), calcite ($CaCO_3$), a silicate gel, an aqueous phase with bicarbonate present, and unreacted CO_2. The volume of leftover CO_2 depends on how long the reaction is allowed to proceed, how much mineral feed is present, and the temperature/pressure conditions. In general, an excess of mineral feed, high temperature and pressure, and longer time for reaction will decrease the volume of unreacted CO_2. This CO_2 can be recycled through the combustion chamber as part of a CO_2/O_2 recycle process, it can be fed through the carbonation chamber again when new feed is introduced, or it can be sequestered underground.

It has been found that the bicarbonate product is critical to the formation of magnesite. As pressure increases, more CO_2 dissolves in water, forming bicarbonate ions. This concentration can be further increased by adding sodium bicarbonate. Bicarbonate ions hydrolyze the silicate minerals forming magnesite, hydroxide ions, and more silicate. This reaction causes the pH of the solution to be approximately 7.7-8.0. In addition, bicarbonate ions are not consumed in this reaction; bicarbonate therefore functions as a catalyst[9]. It is also believed that NaCl, when dissolved in water, provides a complexing ion (Cl^-) that reacts with magnesium ions in solution. This would reduce the free Mg^{2+}, allowing more of the silicate mineral to dissolve in solution, thus increasing the amount of carbonation[10].

Another additive that facilitates the reaction is magnetite (Fe_3O_4). Magnetite offers three benefits: it catalyzes carbonation by forming reaction intermediates, it lowers oxygen levels, thereby suppressing the presence of ferric iron (which can react with Cl^- to form $FeCl_3$), and it can react with CO_2 and magnesium to form iron-bearing magnesite. Recent experiments show that 78% of serpentine used can be converted to magnesite in 30 minutes at 155°C and 18.3 atm with a 0.15 mass fraction of solids in reactants. This did require heat pretreating and fine crushing. Lack of heat pretreating resulted in a very sluggish reaction (almost negligible carbonation after extended periods of time)[8].

If no beneficial additives can be developed, the reaction itself does provide some heat energy. Combining CaO with CO_2 to yield $CaCO_3$ releases 179 kJ/mol. The similar reaction for MgO releases 118 kJ/mol. Therefore, some of the heat necessary for pretreating can be supplied by this process. For comparison, the energy released by combustion of carbon with oxygen to yield CO_2 is 394 kJ/mol. If the heat from mineral carbonation cannot be recycled for dehydroxylation purposes, its energy release is almost comparable to the original combustion process. This can help lower the cost of dehydroxylation[11].

In addition to carbonation of the minerals in solution, magnesium and calcium can be extracted prior to carbonation. Hydrochloric acid, caustic soda, sulfuric acid or steam can be used to separate the desired metals from the minerals. If, for example, serpentine or olivine were dissolved in hydrochloric acid, the silicate compounds would precipitate out. The only products remaining are magnesium chloride and water, which form $MgCl_2 \cdot 6H_2O$ when $MgCl_2$ is hydroxylated by water. Heating this solution boils off the water, regenerates the acid (reforming HCl for later use), and decomposes the magnesium complex to $Mg(OH)_2$. Upon dissolution in water, magnesium hydroxide can be carbonated by dissolved CO_2 to form magnesium carbonate while magnesium chloride can be recycled for acid recovery. In addition, the energy released when serpentine or olivine is dissolved in water is high enough that it sustains boiling temperature, assisting in acid regeneration and minimizing energy input[10]. This process is shown in Figure 13.

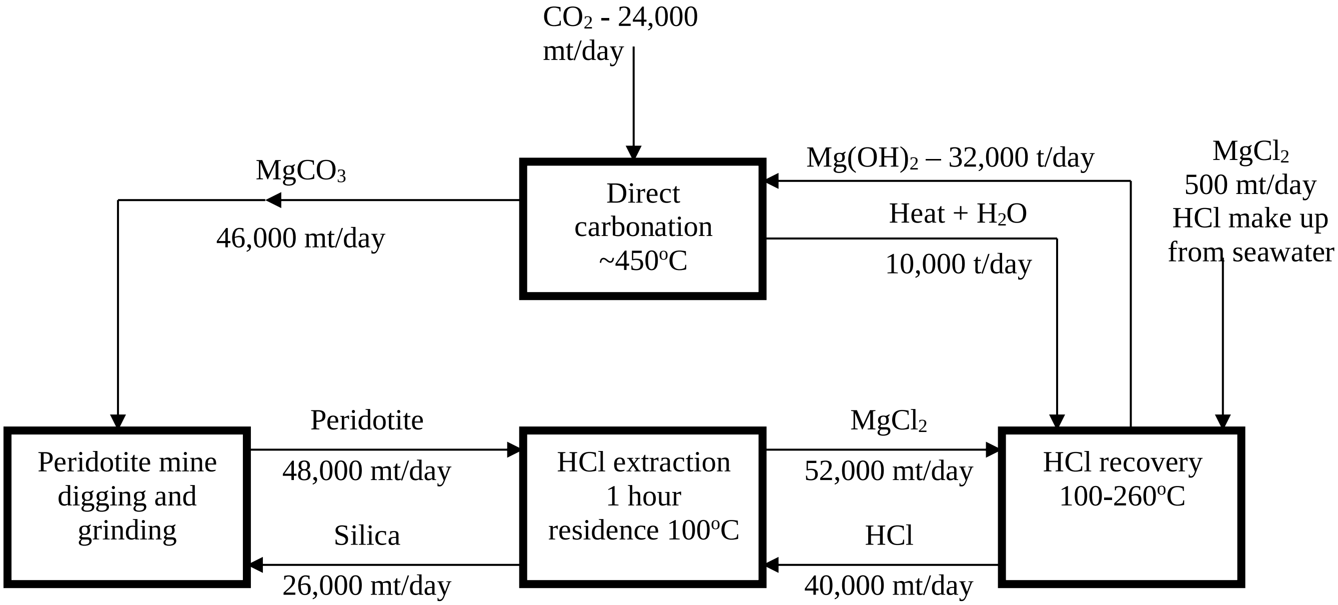

Figure 13 – Aqueous carbonation with acid recovery[11].

Another, simpler, method for direct carbonation is carried out at high temperature with no aqueous interactions. In this process, serpentine or olivine is very finely ground (20 μm size grains[12]) and placed in a high temperature reactor with a CO_2 atmosphere. The purity of this atmosphere is addressed below. The temperature in this chamber must be less than the equilibrium temperature (which is a function of the chamber pressure). For both calcium and magnesium, higher temperature and pressure favor carbonation. However, these conditions can only be raised so far, or the thermodynamically preferred state is gaseous CO_2 (for calcium carbonate, equilibrium conditions are 887ºC at 14.5 psi and 1397ºC at 2901 psi while magnesium carbonate is equilibrated at 407ºC at 14.5 psi and 657ºC at 2901 psi). For example, if the temperature in the reactor is 1450ºC at 2900 psi, gaseous CO_2 will be present instead of carbonated calcium; at 1350ºC and 2900 psi, carbonation of calcium will occur. In one test, the reaction involving magnesium hydroxide reached 8% stoichiometric completion in 10 minutes before leveling off[11]. The heat that is given off by the carbonation is sufficient to raise the reactants to temperatures very close to that necessary for more carbonation, so this process largely supports itself; a supply of CO_2, minerals, and small amounts of heat is all that is needed. This method is relatively simple and the products can easily be disposed of into the original mine, from which the minerals used in the reactor were obtained[10]. A cost analysis has not been performed for this process yet, but if efficient heat exchangers can recycle heat from the products back to the reactants, costs are predicted to be economically acceptable.

The above three methods for direct carbonation all succeed at the primary goal of speeding up the carbonation reaction. While aqueous processes are much more complicated than dry carbonation, they may offer faster reaction rates and are better able to recycle heat given off by the reactions. In addition, most of the steps used for aqueous carbonation are presently used in industry for production of various magnesium- and calcium-bearing compounds. The challenge then is to integrate these different steps into an efficient system close to a point source of CO_2[11].

A general forced mineral carbonation process is shown in Figure 14. The estimated cost for mining, milling, and transporting the minerals is $4.5/ton[1]. The cost of separating and concentrating the minerals adds another $4/ton, bringing the cost for complete preparation to approximately $8.5/ton[11]. In addition to this low transport cost, serpentine and olivine are very abundant and very accessible, especially in Western North Carolina. Also, the energy penalty for actually performing the carbonation has been estimated to be as low as $0.03/kWh (that is, if the price of electricity was increased by $0.03/kWh, a plant would earn the same amount of money as it would without the entire sequestration process). Current electricity costs are approximately $0.045/kWh, so the cost would increase by 66%. This cost translates into $31/ton CO_2 for sequestration. To illustrate the status of sequestration research, the goal for cost is from $10-$15/ton CO_2 sequestered.

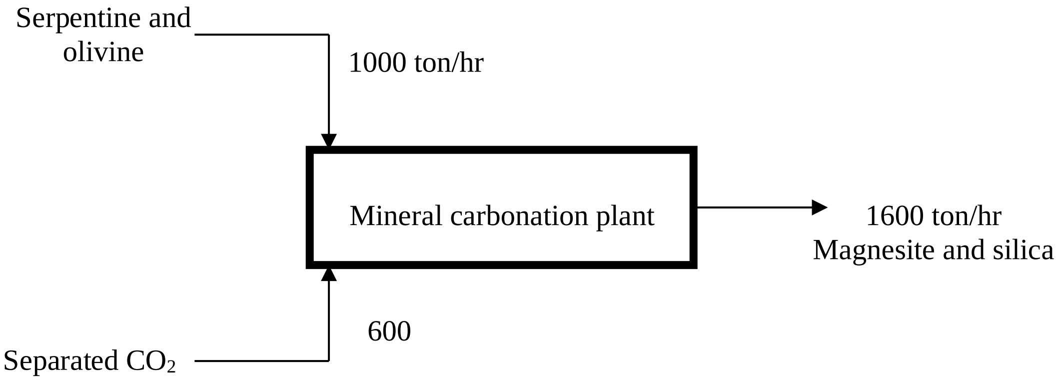

Figure 14 – General mineral carbonation scheme[10].

The main obstacle to this process is that the minerals used (most often serpentine and olivine) must be pretreated prior to dry carbonation. These minerals are silicates that contain magnesium, calcium, and water in their crystal lattices. The water must be removed before dry carbonation can occur at an accelerated rate. This preconditioning occurs after the minerals have been ground to approximately 20µm size; it involves heating the minerals to 600-650°C, inducing an energy penalty of nearly 20% of the total power output of the plant. The reaction is relatively fast (approximately 78% of a sample can be carbonated in 30 min), however, once the minerals are dehydroxylated[10].

Aqueous chemistry (dissolving the reactants in water/acid and carrying out the carbonation in solution) lessens the need for pretreating, but the chemicals used may require more expensive equipment that will not be degraded in the process. Efficient heat exchangers would also be necessary to minimize energy input for acid regeneration[11]. Also, some chemicals will be lost due to degradation in the process, so they must be replenished. Further research is necessary to discover whether any other complexing agents or catalysts can be used that will allow serpentine and olivine to be carbonated without prior dehydroxylation.

One approach to lower the overall cost (including separation) is to sequester a less pure stream of CO_2. Research on this concept is very recent and incomplete. However, it has been found that acid gases such NO_2, SO_4, and H_2S do not significantly affect the rate of mineral carbonation. The presence of SiO_2 (a product from the carbonation reaction) did increase dramatically over time, though, indicating that mineral carbonation was occurring despite the presence of the above named impurity gases. The minerals formed in this process were not limited to magnesite and calcite, either; dawsonite also precipitated out of the solution. Quartz also formed in the reaction vessel. The growth of quartz lowered the dissolved silica concentration. This in turn altered the composition of the solution to favor the formation of more dawsonite, which sequesters more CO_2[13]. The difference between this carbonation rate and the rate of carbonating pure CO_2 streams has yet to be ascertained.

Coal Bed Adsorption

Adsorption of CO_2 by a coal bed for sequestration and methane gas recovery is another option, especially attractive due to the large amount of coal in the Tennessee Valley and the recovery of methane (useful in energy production). Since CO_2 is more interactive with coal than methane, methane is displaced and CO_2 adsorbs onto the coal. Physical adsorption is the mechanism upon which this process operates. No chemical interactions are relied upon for CO_2 to be sequestered on coal beds.

Research has shown that increased pressure facilitates adsorption (similar to CO_2 separation by adsorption)[14]. Higher temperatures, however, decrease adsorption capacity. This is due to the fact that, at higher temperature, gas molecules have higher energy, leading to desorption (analogous to trying to catch a high energy speeding bullet vs. a low energy football). Deeper coal beds (deeper than the 2625 ft average) are typically warmer, so they are predicted to not adsorb as much CO_2[15].

Helium is often used to estimate the volume of CO_2 that can be adsorbed by coal in experiments; however, estimates of CO_2 capacity are lower than the true capacity of a specific coal. This is because coal swells as CO_2 is adsorbed onto it. As the coal swells, more volume is made available for adsorption. This leads to the assumption that more CO_2 can be sequestered on coal beds than previously anticipated[16].

Current estimates agree that approximately 40 Gmt CO_2 can be sequestered in the U.S. alone as part of methane recovery applications in unmineable coal seams at costs similar to other underground sequestration processes[1]. The cost to implement this process is comparable to that for injection into a saline aquifer. This method for sequestration is still very new and needs further research to optimize the conditions that favor adsorption.

Purity of Injected CO_2

In addition to the production of methane, sequestering CO_2 in unmineable coal seams allows the degree of CO_2 separation to be less than pure. When N_2 is pumped into a coal seam, rapid displacement of methane occurs. The N_2 does escape after a period of time, however, less than 20 years. If a mixture of CO_2 and N_2 were pumped into a coal seam, rapid methane production would occur because both gases adsorb onto coal with greater attraction than methane. N_2 strips methane from coal as it is injected because the partial pressure of gaseous methane decreases. As it decreases, sorbed methane gasifies to restore the equilibrium pressure[17]. CO_2, however, is more strongly sorbed by coal than methane or N_2, so it simply displaces the other gases. Once N_2 desorbs (after it has already replaced the methane), more CO_2 can be sequestered in its place. The advantage of this behavior is that N_2 does not have to be separated from a flue gas stream prior to injection, thus lowering the cost for separation. This could be a drastic reduction since N_2 comprises approximately 80% of flue gases while CO_2 makes up 15% (depending on where the separation unit is located)[18]. In addition, all of the CO_2 injected will eventually adsorb onto the coal; some CO_2-N_2 recycle would be necessary, as a mixture with CO_2, N_2, and rich in methane would be produced.

This process does cause a methane purification step to be necessary. After methane production begins, N_2 will eventually begin to escape from the coal. It would then mix with the methane, decreasing its purity. Investigation regarding the amount and cost of this purification will reveal whether this process will be economically viable. Methane is a more active greenhouse gas than CO_2 (it holds more energy, thus raising temperature more than CO_2); if the methane from this process is not used, it must be sequestered somewhere else since its effect on the atmosphere is worse than that of CO_2. Release of methane into the atmosphere would defeat the purpose of sequestering CO_2[19].

Effects of Acid Solution

One method that could possibly increase the capacity of coal is to wash it with acid, such as H_2SO_4 and H_2NO_3. Research has shown that acid-washed coals adsorb significantly more CO_2 when pressure is above 600 psi. Pressures below this do not exhibit as great a degree of difference whether coal is washed with acid or not. This can lower front-end separation costs if acid gases such as NO_x and SO_x are used to make the acid for washing. The contributions of micro- and mesopores to CO_2 adsorption appear to increase with acid washing as well[20]. Lower pH from the use of the acid gases also causes calcite to dissolve into solution. This can be beneficial if it only opens up the pores; however, if the acid dissolves cap rock formations, leaks can occur, rendering useless the sequestration operation.

Another concern that must be addressed is the effect of microbes that grow in coal seams. These microbes have been found as deep as 9000 ft and can alter conditions in the seam. Under oxic conditions (conditions with oxygen that allow sulfur, nitrogen, and carbon to react with oxygen to form acid gases) acid gases such as SO_x, NO_x, and CO can be produced; anoxic conditions (little free oxygen available for reaction) stimulate the production of methane and H_2S. These gases could displace sorbed CO_2 or contribute to the acidity of the solution[21]. Increasing the acidity of the solution too much could dissolve some rock formations, compromising the seal on the formation.

Injection Equipment and Procedures with Preconditioning

Injection can be performed via wells drilled into the ground and open into a deep coal seam (seams too deep to mine) or saline aquifer. These wells must be carefully placed and drilled so that fracturing does not occur. Prior to injection, CO_2 must be cooled enough so that the energy of the gas molecules is low enough for adsorption; the amount of cooling depends on the separation process used to separate CO_2 from flue gas. After cooling, the CO_2 must be pumped down the well into the seam where adsorption or mineral carbonation occurs. As the gases are pumped into the ground, the gas equilibrates with the temperature and pressure in the formation. The chamber in which the gases are stored can be pressurized as long as the fracturing pressure is not exceeded. The fracturing pressure must be approximated based on the structural stability of the formation. More powerful injection pumps are necessary for this “over pressurization.”

It is typical for multiple wells to be drilled to one coal bed or aquifer if the formation is large enough. Without multiple wells in a large formation, the gases would slowly diffuse through the formation forcing injection to be slow or pressure to build up near the well. Pipelines from the CO_2 source are necessary for feed supply. This should not be a large cost issue if the power plant is located close to the coal bed or underground aquifer. Instrumentation is also necessary to monitor temperature, pressure, formation water flow, and other relevant parameters. All of this equipment (pipeline, pumps, coolers, wells, monitoring instrumentation, data acquisition systems, etc) is similar to that used for oil extraction since injection was originally a method for EOR.

Separation Technologies

The most promising methods for CO_2 separation are membrane separation and the Mitsubishi process for chemical absorption. Both processes involve separating CO_2 at relatively high temperature, reducing the cost for cooling prior to separation. In addition, high temperature favors the supercritical state of CO_2. Some cooling may be preferable if transportation equipment is more stable at lower temperature. A heat exchanging system can be installed to cool exiting gases to the injection temperature. The injection temperature depends on the equipment used for transportation of the CO_2. For example, the material used for a pipeline may not be able to withstand high temperatures and concentrations of CO_2 in the separated gas. Heat exchangers can be installed that remove heat from the exiting CO_2-rich gas; the waste heat from the heat exchanger can be used either for a separate steam power generator in a membrane application or regeneration of solvent in the Mitsubishi process. Also, if CO_2 is to be stored at a great depth, high-pressure pumps will be necessary to overcome the pressure of a formation (either coal or saline aquifer). The degree of CO_2 separation from flue gas required for injection has yet to be fully addressed (see explanation above).

Due to the geologic time scale sequestration periods, relatively safe conditions, general proximity to point CO_2 sources, and extensive prior knowledge of underwater formation water flow, sequestration of CO_2 in underground aquifers and coal beds is a very promising method of mitigating greenhouse gas emissions. The cost is predicted to be relatively low and the suitable sites are numerous for this application, with many of these sites located close to the plants.

Suggested CO_2 Process for Pilot Testing Geosequestration

Based on the review of the currently available processes for the separation of CO_2 from flue gas that was discussed in Section I and the requirements for the thermodynamic conditions of CO_2 before injection discussed in this section, Figures 15 and 16 illustrate the suggested separation unit type and placement for a pilot plant. In Section I, ceramic and/or metallic membranes were chosen as the best method for separating CO_2. However, acceptable materials that are ready for pilot testing have not yet been developed.

Separation by chemical absorption is therefore the process of choice. A drawback to chemical absorption is that cooling the flue gas is required prior to separation, even when the unit it placed at the stack (approximately 100°C cooling is required). Two relatively simple solutions exist to cost-effectively cool the flue gas to separation temperature. First, a heat exchanger can be installed between exiting separated CO_2 and incoming flue gas (Figure 16). This is desirable because the flue gas must be cooled for separation while the separated CO_2 must be heated above its critical temperature before underground injection. A temperature difference of 650°C exists between these two streams, facilitating heat transfer. The second solution is also shown in Figure 16; a chilled water system removes heat from the gas stream at various points. The cooled water point that occurs after liberation of CO_2 is not necessary, since the next step after separating CO_2 is to heat it to its critical temperature. Of course, some extra cost will be incurred to cool the water. Once the desired purity of CO_2 has been reached (the amount of N_2 left in the CO_2 stream is discussed above), the gas can be sent through the heat exchanger for injection temperature preconditioning. For geosequestration in an underground aquifer, supercritical CO_2 is the best state (the critical point for CO_2 is 31.1°C and 73 atm). It can be seen in Figure 15 that the CO_2 leaving the separation unit leaves at ~110°C (if the cooled water heat exchange is not included). The heat exchanger proposed above would heat the CO_2 even further; this, however, will produce no negative effect, since the supercritical state depends only on exceeding the critical temperature. The exiting pressure of the separated stream is much lower than the critical pressure (1 atm instead of 73 atm), thus requiring significant compression to achieve the supercritical state. Powerful compressors and pumps and strong transport pipelines will therefore be required. Once the CO_2 has been heated and compressed to meet or exceed critical conditions, it can be pumped via pipelines to the sequestration site. Insulation would be necessary for the piping to retain heat in the CO_2 stream. Reheating at the injection site may not be necessary since the heat exchanger between the exit CO_2 and inlet flue gas can heat the CO_2 well beyond its critical temperature.

Information regarding purity of the CO_2 stream injected into an underground aquifer was not found. Since the injected stream should exceed supercritical conditions for CO_2, any N_2 in the stream will be supercritical as well (its critical temperature and pressure are –146.9°C and 33.5 atm, respectively). The effect of supercritical N_2 on formation water and dissolution of CO_2 was not found in the available literature. If the stream is injected into a coal seam, however, it is known that N_2 does not really affect the adsorption of CO_2. When a mixture of the two gases is injected into a coal seam, N_2 rapidly adsorbs to the coal, but it leaves as CO_2 builds up. Because of this behavior, a mixture could be injected and the N_2 that desorbs allowed to escape to the atmosphere. The main concern here is that methane trapped in the coal is also liberated. When the CO_2/N_2 mixture is injected, both gases quickly displace methane. Thus, methane and N_2 begin to build up above the coal seam while CO_2 is adsorbed. It is possible to harvest this methane for commercial use, but a separation between methane and N_2 would then be required. The economic feasibility of this methane harvesting has not yet been investigated.

While the MHI and Econamine FG™ solvents are believed to be the best solvents currently available, these are not yet commercial products. Use of a readily acquired, cost-effective, and traditional solvent is therefore recommended for near-future application. MEA has been used for over 60 years, so its behavior and capacities are very well known and understood. Until new solvents are easily procured, MEA is most likely the best solvent to use. Drawbacks to using this solvent include that it degrades relatively easily if too much O_2, SO_x, NO_x, or fly ash is present. The SCR, ESP and FGD in the pilot plant must be very efficient in removing these components to minimize solvent loss. Also, regenerating MEA imposes a substantial energy penalty on the plant, due to the amount of energy required to liberate CO_2 from the MEA. Equipment that is able to withstand high regeneration temperatures and chemical corrosion will be necessary. However, efficient heat exchangers can lower the regeneration penalty by minimizing fuel use. While this will be a costly process, the introduction of new solvents should be relatively easy. Most likely the required equipment will be the same or very similar, so minor retrofitting will be necessary as new solvents become available.

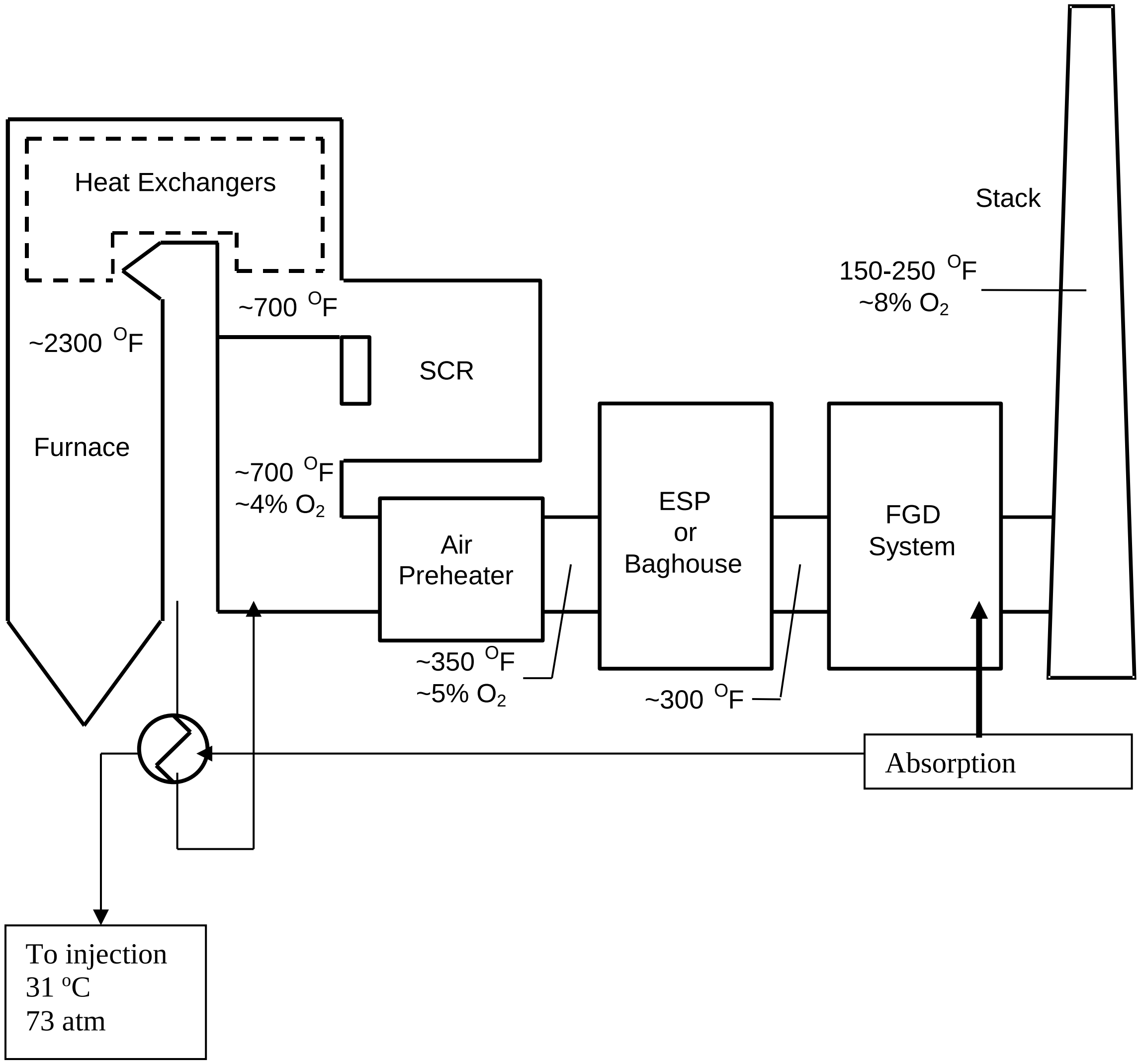

Figure 15 – Placement of Absorption Separation Unit.

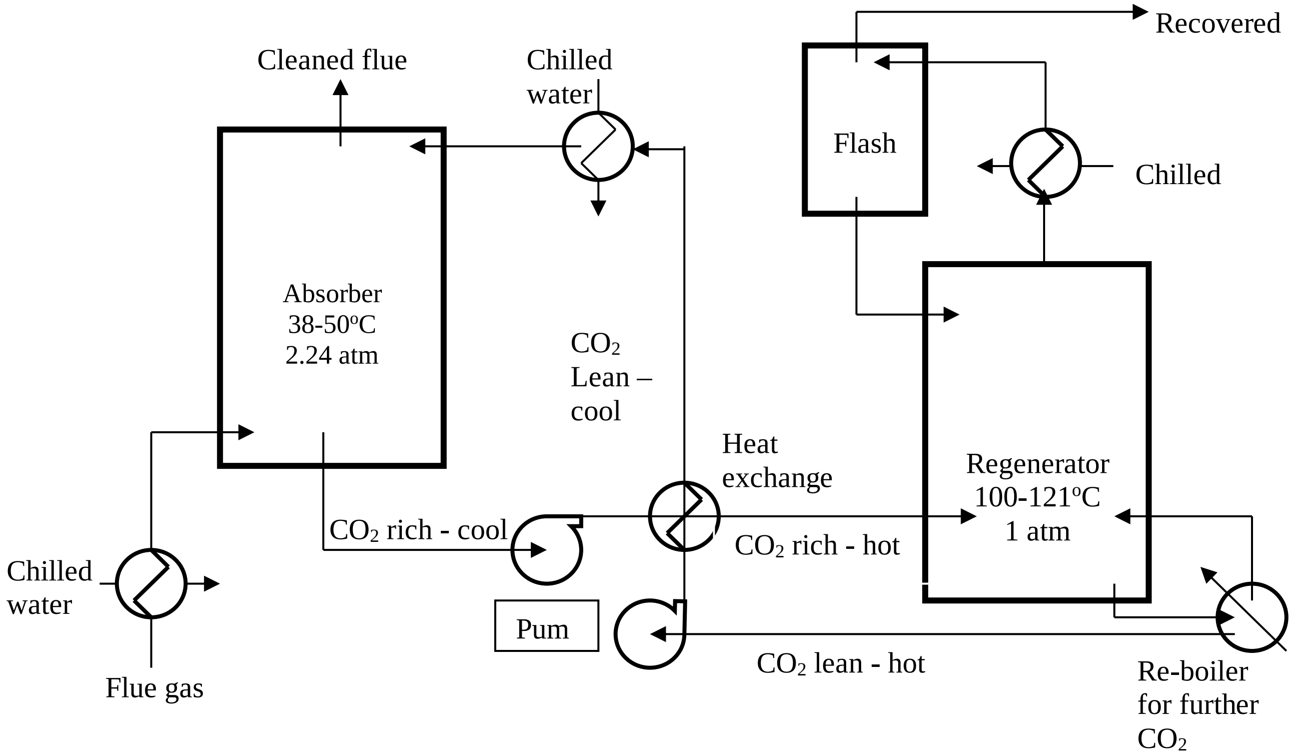

Figure 16 – Separation Process for Pilot Plant.

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III. POTENTIAL FOR ONSITE GEOLOGIC SEQUESTRATION OF CO_2 AT TVA FOSSIL PLANTS IN THE SOUTHEASTERN U.S.

Introduction

Eleven TVA fossil fuel-burning plant locations were evaluated for the potential for onsite geologic sequestration of CO_2 from stack emissions. These sites, shown in Figure 17, include: the Shawnee and Paradise plants in Kentucky; the Allen, Johnsonville, Cumberland, Gallatin, Kingston, Bull Run, and John Sevier plants in Tennessee; and the Widows Creek and Colbert plants in Alabama. The suitability of a site for deep CO_2 injection depends on a number of geologic, hydrologic, economic, and socio-political factors (Bachu, 2000; 2002; van der Meer, 1993; Bergman et al., 1997), all of which must be taken into account. For this study, evaluation of the 11 TVA sites utilized a set of selection criteria to rank the sites in terms of their estimated suitability for onsite CO_2 injection. These criteria, described in the next section, include the following:

1. Basin origin and tectonic setting
2. Regional scale geology, lithology, and hydrostratigraphy
3. Known oil, gas, and coal reserves.
4. Depths to the 32º C isotherm and 7.4 MPa isobar
5. Hydrodynamic regime
6. Permeable and porous zones for injection and sequestration
7. Economic considerations (e.g., potential for hydrocarbon recovery, existing infrastructure)
8. Socio-political considerations
9. Availability of data

Criteria 1-8 are based on Bachu (2000) and the ninth criterion was added in recognition of the wide variation in data that is readily available for site evaluation. Where very little information is available, there is a risk involved in the investment of time and resource on detailed site characterization in the absence of a strong indication that sequestration potential exists.

Some assumptions were used to assess the sequestration potential. First, it was assumed that sequestration would occur within close proximity of the site and, therefore, the evaluation was restricted to the site locations. Second, it was assumed that the injection interval would be at depths sufficient for meeting the pressure and temperature conditions necessary for CO_2 to be in the supercritical phase. Under these conditions, CO_2 behaves like a gas but has the density of a liquid, making sequestration more efficient and cost-effective. Finally, average hydrostatic pressure and geothermal gradients and an average surface temperature were assumed for determining the depth to supercritical conditions for CO_2.

It is important to state that this study does not attempt to quantify the storage capacity at any of the sites. Neither the available data nor the scope of this effort are sufficient to support that level of detail. What this study does provide, however, is a prioritization of sites for future in-depth evaluation and a summary of the readily available information for each of the sites that provided a basis for prioritization. Primary sources for information include the U.S. Geological Survey, the Geological Survey of Alabama, the Kentucky

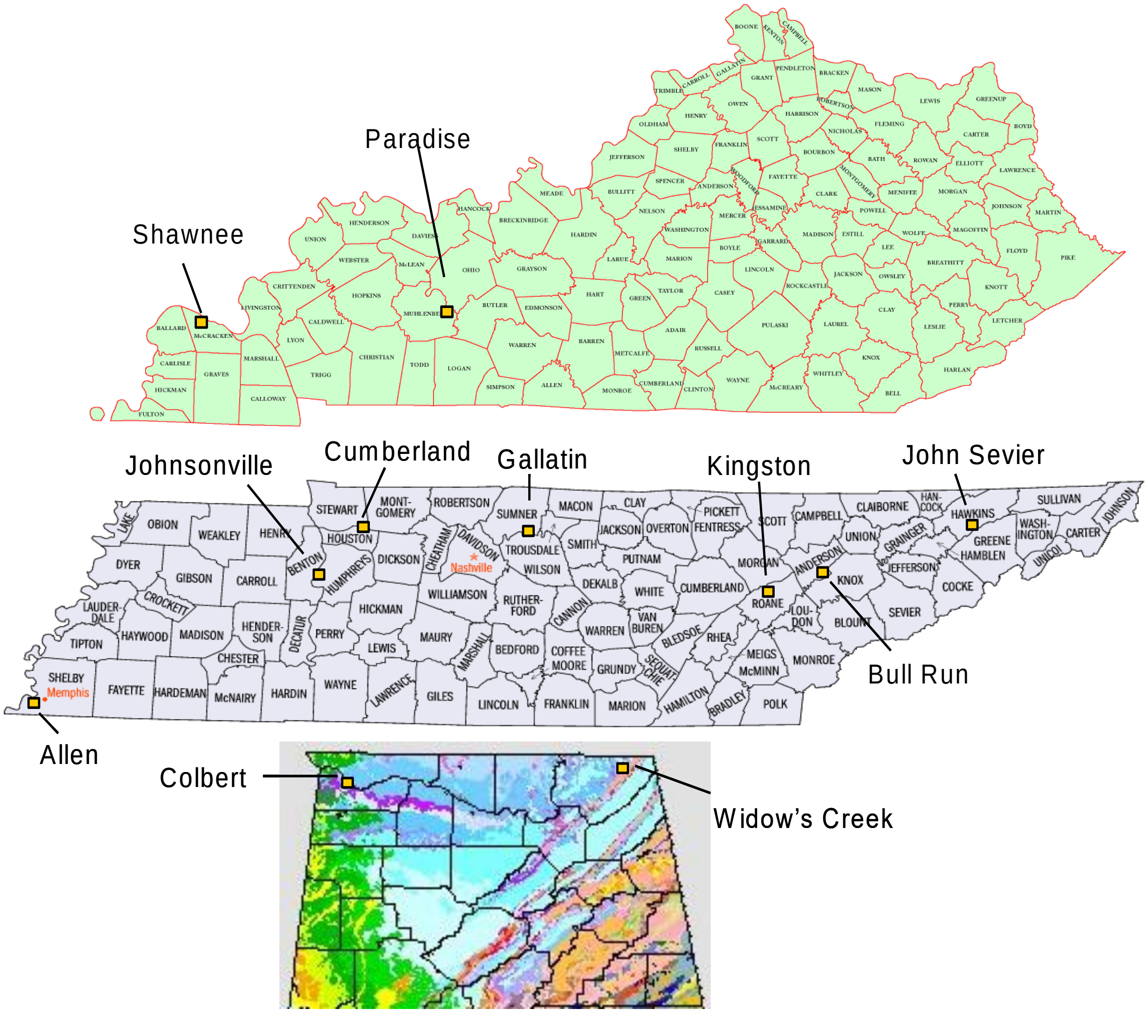


Figure 17. Locations of the eleven TVA coal-fired plants included in this study superimposed on county maps of Kentucky and Tennessee and on a geologic map of northern Alabama.

Geological Survey, the Geology Division of the Tennessee Department of Environment and Conservation, and TVA. Information obtained from these sources includes fossil plant engineering reports, geologic maps, well logs and driller's logs, hydrostratigraphic classification, coal field distributions, oil and gas well locations, and regional and local aquifer distributions. In most cases, this information is generalized over large regions. Site-specific, detailed information requires deep well penetrations within sufficient proximity that extrapolation is possible, and in most cases this was not available through the sources listed above. Even where well drilling records are kept at state survey offices, much of the information that would permit evaluation of potential subsurface injection targets, such as pressure tests or core permeability tests, was not available. It is possible that additional detailed reservoir information could be obtained from gas and oil field operators, mine operators, and industries like DuPont that have evaluated sites in close proximity to some of the TVA sites for petroleum resources, coal resources, and deep waste injection potential, respectively. This possibility was factored into the ranking for potential sequestration sites.

This report is organized into three primary sections. In the first, the selection criteria as they pertain to this evaluation are discussed and regional-scale information is presented that places the sites within a larger tectonic and hydrodynamic framework. The second section is a site-by-site description of the 11 TVA fossil plant locations that gives information on a more local scale and identifies the favorable and unfavorable characteristics with regard to sequestration potential. Thus, the presentation of information will move from regional scale to local scale. The final section is an appendix that contains a listing of data sources by location that can become the starting point for a more in-depth evaluation at a site selected for the development of a field test facility.

Evaluation and selection criteria

The sequence of evaluation and selection criteria generally progresses from larger scale features that control regional hydrodynamics and storage capacity to increasing local detail. By following this sequence, sites can be prioritized for retention or elimination from initial consideration, thus focusing the effort on those sites exhibiting the greatest suitability for CO_2 sequestration.

Basin origin and tectonic setting

The potential sequestration site needs to be assessed according to the tectonic setting in which it is located in order to evaluate the risk of rapid escape of large amounts of CO_2 that could pose an environmental or health and safety risk. The tectonic setting refers to the past and present movement of crustal plates that has resulted in large-scale geologic features formed as a result of the forces associated with plate movement. Regions associated with convergent plates, such as the west coast of the U.S., are prone to significant seismic activity, faulting, or volcanism and should be avoided as potential sequestration sites. Generally, divergent basins on stable continental platforms, particularly foreland and intracratonic basins are best suited due to their relatively stable tectonic characteristics (Bachu, 2000). Figure 18 shows the relationship of the TVA fossil plant locations to major tectonic features. These features control the surface expression of geologic formations and the distribution of regional aquifer recharge and discharge zones.

The land surface is divided into physiographic provinces, regions in which the surface geologic characteristics are an expression of tectonic events such as continental collisions or rifting. Physiographic provinces are indicative of large-scale subsurface structural features and overall tectonic stability. For example, the Valley and Ridge province is comprised of a series of parallel ridges and valleys that resulted from a series of thrust faults that developed during the creation of the Appalachian Mountains. As slabs of strata were thrust on top of each other due to compressional forces, a repeating sequence of rock strata was created. More intense erosion of the less resistant layers (e.g., shales) produced the pattern of ridges and valleys seen today. Other physiographic units are represented by major domes or ridges and basins.

These relationships are further illustrated in Figures 19 and 20. In Figure 19, the TVA fossil plant locations superimposed on a physiographic map of Tennessee. Although the map includes only Tennessee in detail, the physiographic provinces extend northward and southward into Kentucky and Alabama, respectively. Thus, the plants in those two adjacent states can be placed within their respective province by extrapolation due to their proximity to the Tennessee border. The map indicates a diversity of geologic environments within which the plants are located. The nature of these environments and the complexity of associated subsurface structures can be used as a first order selection criterion.

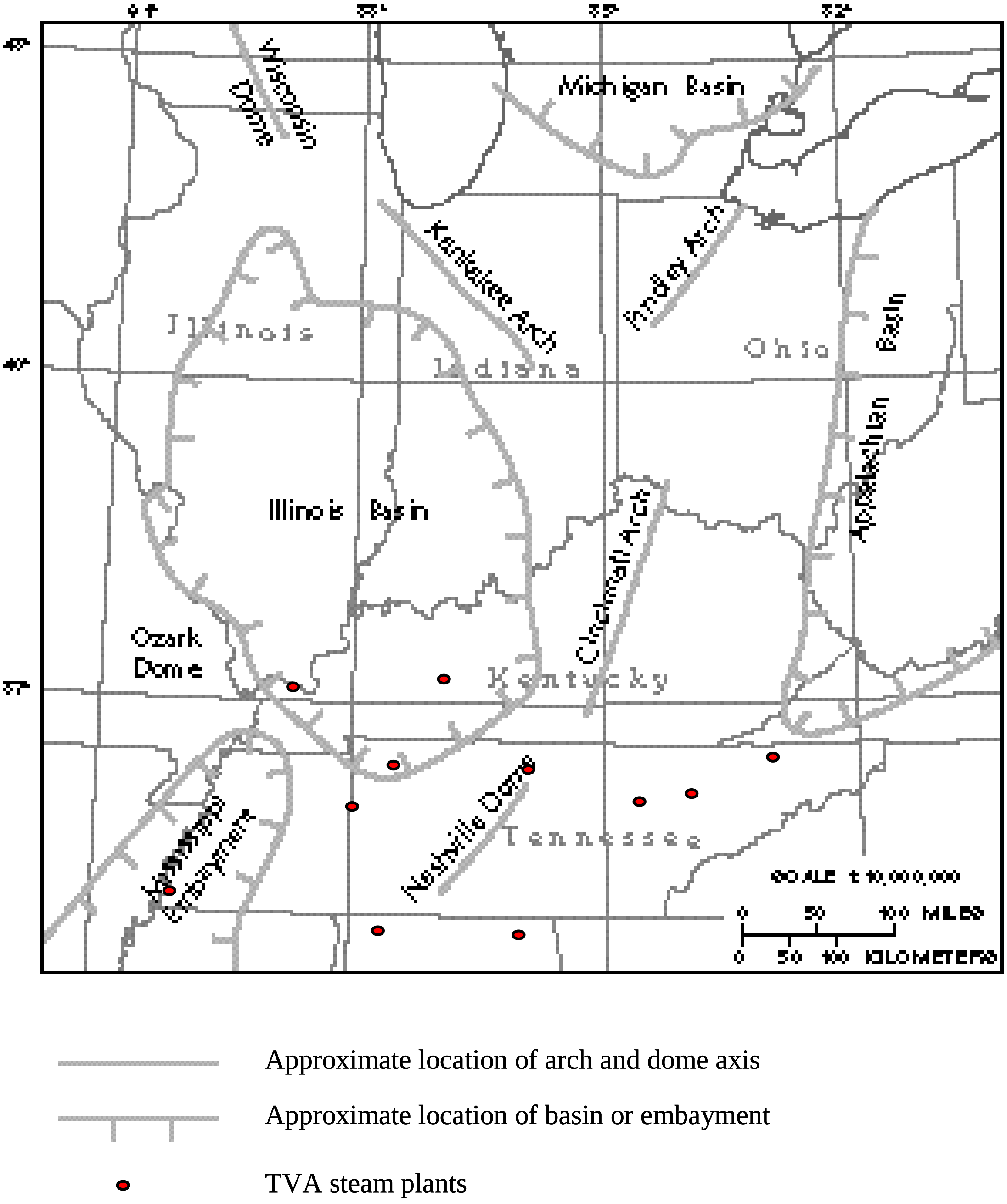


Figure 18. The arches, domes, and structural basins in Precambrian rocks and in the overlying Paleozoic sedimentary rocks this region were created by tectonic forces. Aquifers in the Paleozoic sedimentary rocks are near the land surface over the arches and domes and are deeply buried in the basins. (From Lloyd and Lyke, 1995; modified from U.S. Geological Survey and American Association of Petroleum Geologists, 1962, Tectonic map of the United States: U.S. Geological Survey, 2 sheets, scale 1:2.500.000.)

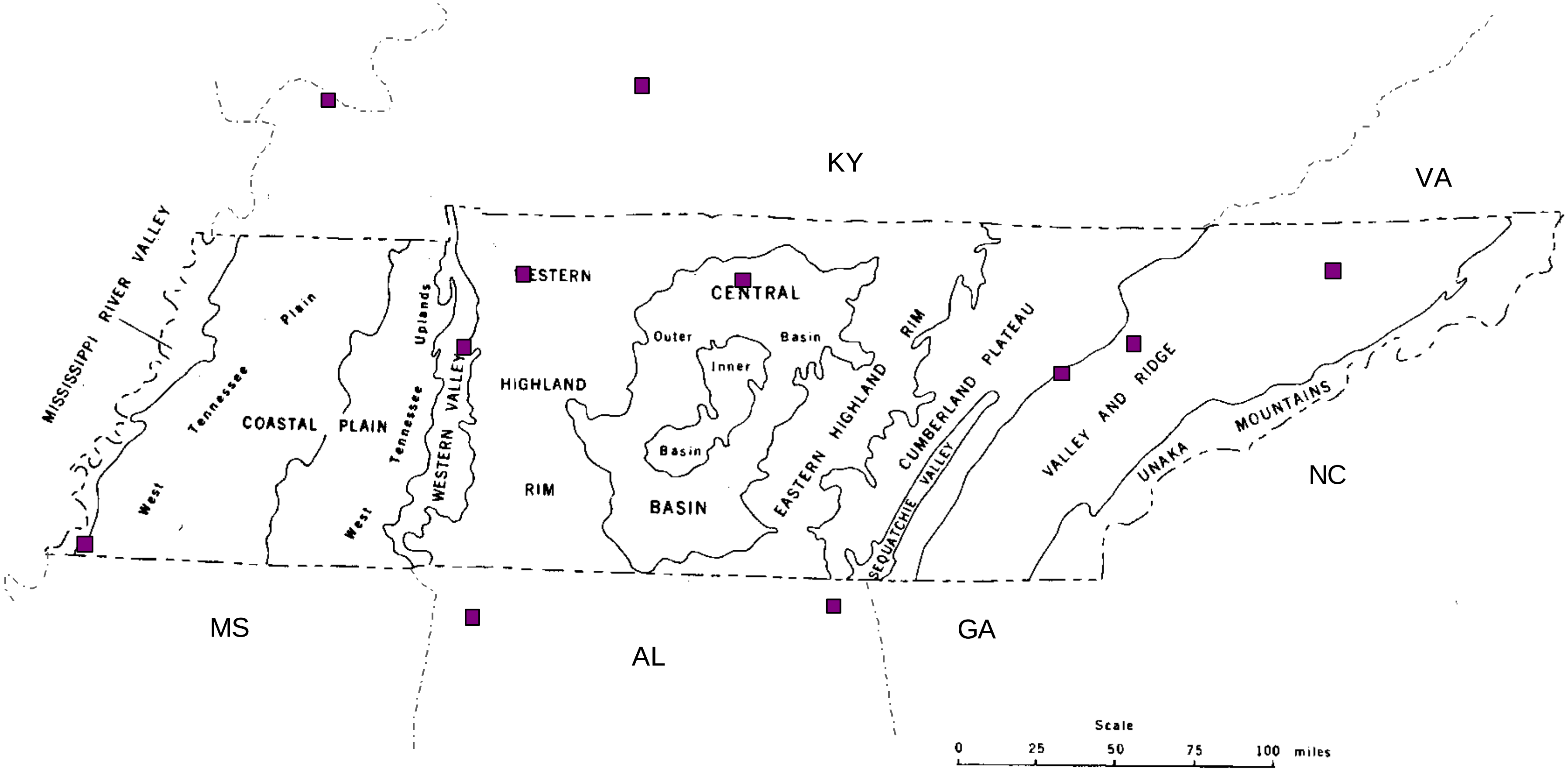


Figure 19. Location of the eleven TVA fossil plants relative to the physiographic regions. The Widows Creek plant in northeastern Alabama is located within the Sequatchie Valley, which is considered part of the Valley and Ridge province due to the structural similarities.

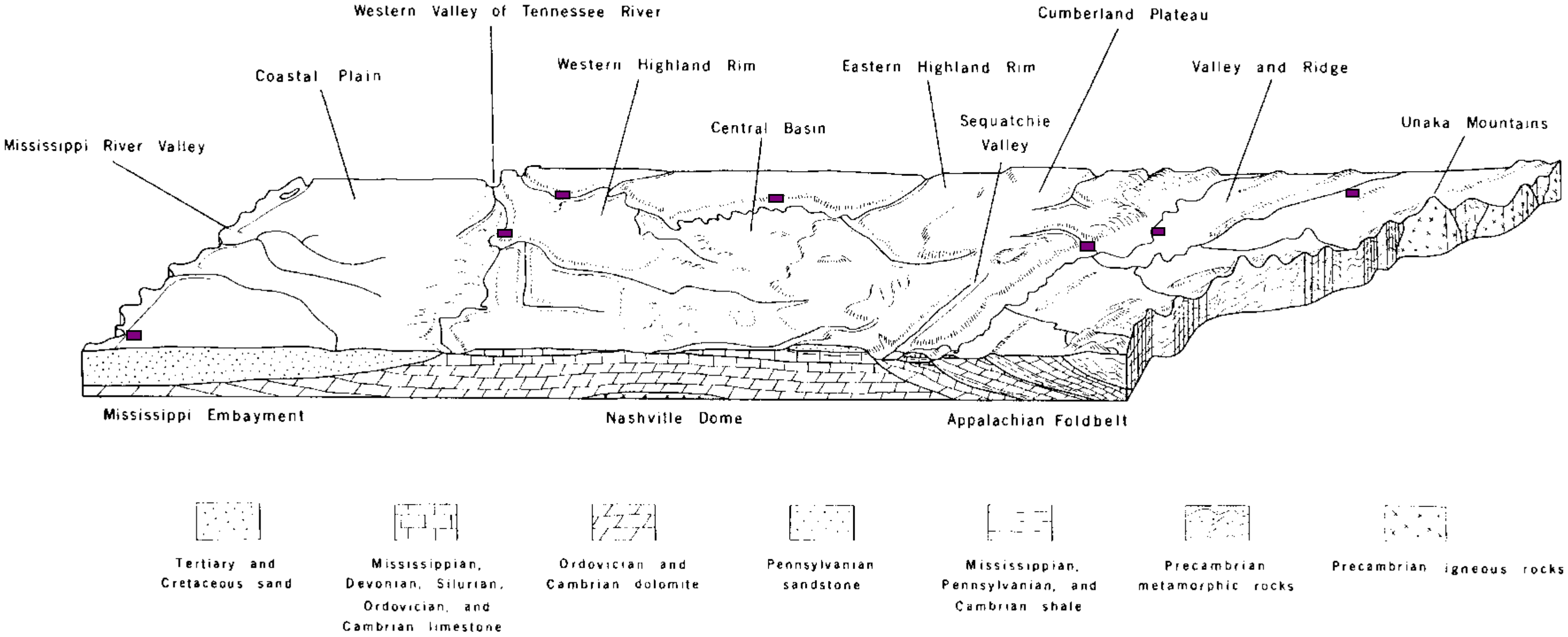


Figure 20. Block diagram of the physiographic provinces across Tennessee showing the relationship to underlying structure. By extension, the features are similar in southwestern Kentucky and northern Alabama. TVA fossil plant locations are identified.

For example, the Eastern and Western Highland Rims, Central Basin, and Cumberland Plateau, all associated with the Nashville Dome, are tectonically stable regions with a lesser degree of local or regional deformation. These regions are underlain by the near-horizontal to gently-dipping strata of the Nashville Dome (Figure 20). The Valley and Ridge, underlain by the Appalachian foldbelt, has undergone intense deformation, making extrapolation of existing geologic information and interpretation more complicated. Large-scale faults may act as seals, preventing extensive lateral movement and providing traps for injected CO_2, or as conduits, providing a means for escape of sequestered gases to overlying strata or even release to the atmosphere. In addition to faults, the dip of rock layers can influence whether or not a subsurface target is suitable for CO_2 storage even in the presence of sufficient porosity. Steeply-dipping beds can provide a pathway for upward migration of sequestered gases. Thus, gently-dipping to flay-lying beds are preferred.

The Coastal Plain and Mississippi River Valley regions are underlain by thick sequences of relatively high-permeability Tertiary and Cretaceous sediments and lie within a zone of regional groundwater discharge. This can increase the potential for upward migration of injected CO_2 across permeable rock layers resulting in contamination of overlying aquifers or release to the atmosphere unless an extensive confining layer is present above the injection target. The Mississippi Embayment is associated with the New Madrid Fault Zone, a zone of incomplete rifting that occurred in the geologic past. The region is considered to be tectonically stable (in comparison to seismically active areas of the Western U.S.), although a major seismic event centered in that fault zone occurred during the 1800's.

Based strictly on tectonic setting, those TVA fossil plant locations underlain by the Nashville Dome and its associated stable platforms and on the flanks of the Illinois basin are the most favorable sites (e.g., the Johnsonville, Cumberland, Gallatin, Colbert, and Paradise plants). The least favorable sites are those underlain by the structurally complex Valley and Ridge province (e.g., the Widows Creek, Kingston, Bull Run, and John Sevier plants). Those located within the Mississippi Embayment are moderately favorable (e.g., Shawnee and Allen plants).

Regional scale geology, lithology, and hydrostratigraphy

Regional scale geology, lithology (rock type), and hydrostratigraphy (rock sequences designated as aquifers or confining units based on permeability) are all interrelated and dictate whether or not the gross subsurface characteristics are favorable for sequestration. All are influenced by the tectonic setting as described in the previous section. In order for sequestration to be viable, there needs to be sufficient porosity and permeability in some of the reservoir rocks, and there needs to be an overlying confining unit to prevent upward migration of the gas injected. Aquifers and confining units both need to be laterally extensive, in the absence of faults or some other structural confinement. Although the term aquifer is often used to designate a source of potable (drinking water quality) groundwater, in this report it will refer to any water-bearing rock unit with sufficient permeability to produce water irrespective of the quality of that water.

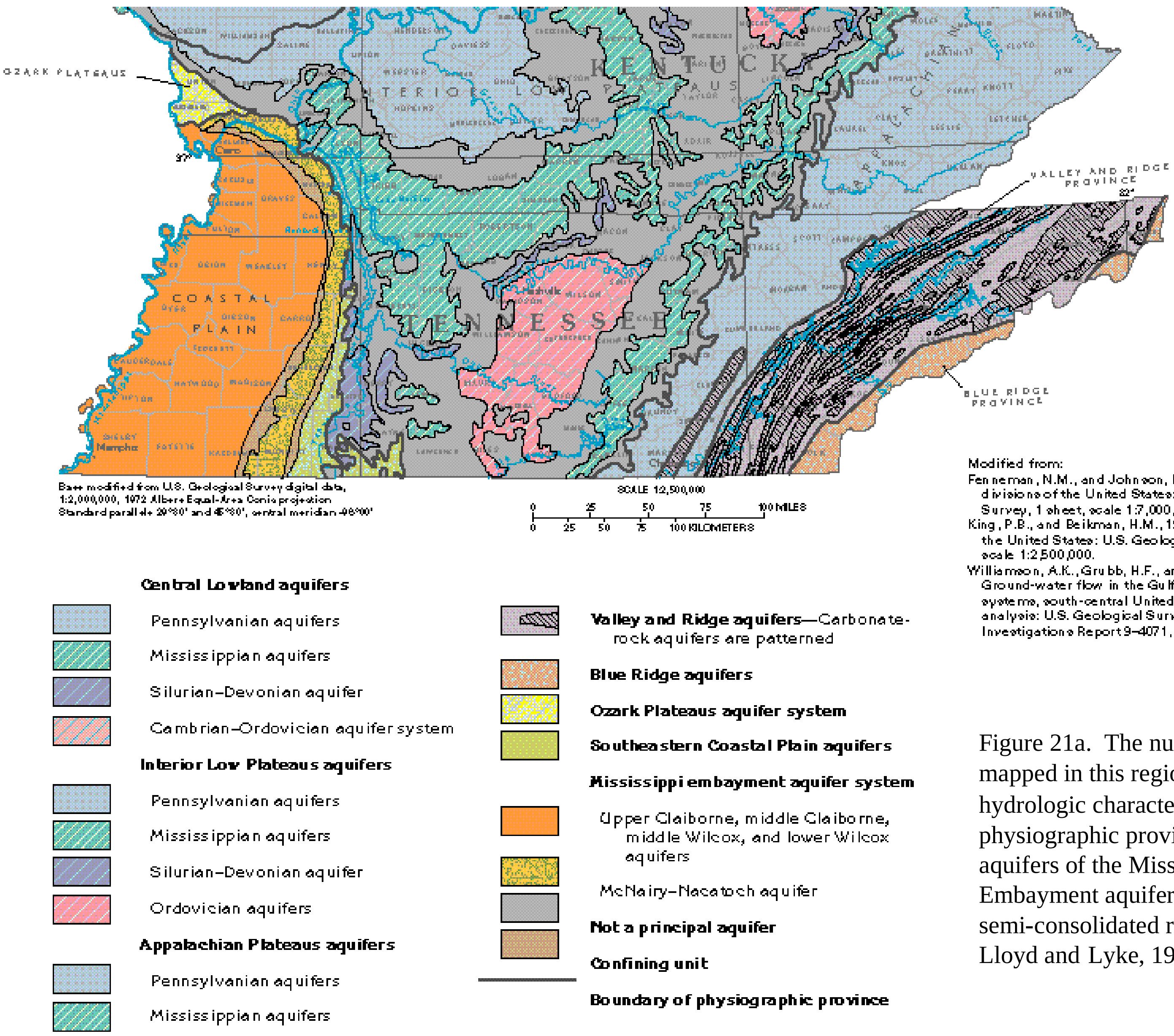
Generally, municipal and private drinking water sources originate from surface water bodies (lakes and rivers) or shallow groundwater aquifers having concentrations of total dissolved solids (TDS) less than 1000 mg/L. Although these freshwater sources occur at shallower depths than those of interest for CO_2 injection, contamination due to upward migration of the injected CO_2 is a concern. Groundwater quality could be impacted either by non-CO_2 components of the injected gas stream or by acidification resulting from increased concentrations of dissolved CO_2 that, in turn, could lead to mineral dissolution and increased TDS. Therefore, it is important to include the potential impact to drinking water sources in the evaluation process. Long migration pathways afford greater potential for dilution of dissolved CO_2 due to dispersion and mixing during groundwater transport. The larger the vertical and lateral separation between drinking water sources and the injection target, the greater the safety factor.

Figures 21a and 21b show the surface distribution of the major aquifer systems by physiographic province and geologic age. The classification of geologic formations into aquifers or confining units is based on their characteristics at surface or near-surface conditions (down to the depth of a groundwater well). As a rule, porosity and permeability decrease with depth due to compaction and diagenetic processes that result in mineral precipitation. Facies transitions can change the characteristics and therefore the classification of a formation from one location to the next. However, the hydrostratigraphic classifications shown in these figures do provide a preliminary means for identifying potential aquifers and confining units at deeper locations. The surface distribution also helps to define recharge and discharge zones for the major aquifers which can assist in determining regional hydrodynamics and potential environmental threats to drinking water sources.

For this study, only the Interior Low Plateaus, Appalachian Plateaus, Valley and Ridge, and Mississippi Embayment aquifer systems are of interest based on location of the TVA fossil plants. The next series of figures (Figures 22-30) shows the surface distribution and hydrostratigraphic columns for each of these four systems, with the TVA fossil plant locations identified on the maps. Placement of the sites within a regional-scale hydrodynamic regime is necessary, however, as the flow of deep formation waters is more likely to be controlled by large-scale structures such as those shown in Figure 18 rather than the local features that control hydrodynamics in shallower aquifers. The details of these figures as they pertain to individual sites will be discussed in the site descriptions below.

Known oil, gas, and coal reserves

Knowing the location of gas, oil, and coal reserves is important for several reasons. First, information gathered during the exploration and production/mining of these resources can provide a valuable subsurface database including downhole geophysical logs, cores, permeability and pressure test data, and seismic data that can aid in evaluating the sequestration potential for a nearby site. Second, the infrastructure created during these activities (e.g., deep test wells, monitoring wells) can potentially be utilized for CO_2 injection and monitoring, reducing the cost of instrumenting a sequestration site. Third, there is potential economic gain from enhanced oil and gas recovery or coal bed methane recovery that can offset some of the cost of CO_2 separation and sequestration. Finally, the concern about contaminating a currently-producing oil or gas field (or one that has yet to be developed) due to migration of injected CO_2 needs to be considered. In this case, contamination would be due to the addition of gases that would be produced with the oil or gas and would subsequently need to be stripped out of the hydrocarbon.



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Fenneman, N.M., and Johnson, D.W., 1946, Physical divisions of the United States: U.S. Geological Survey, 1 sheet, scale 1:7,000,000.
King, P.B., and Beikman, H.M., 1974, Geologic map of the United States: U.S. Geological Survey, 3 sheets, scale 1:2,500,000.
Williamson, A.K., Grubb, H.F., and Weiss, J.S., 1990, Ground-water flow in the Gulf Coast aquifer systems, south-central United States—A preliminary analysis: U.S. Geological Survey Water-Resources Investigations Report 9-4071, 123 p.

Figure 21a. The numerous aquifers mapped in this region vary in their hydrologic character in different physiographic provinces. Most aquifers of the Mississippi Embayment aquifer system are in semi-consolidated rocks. (After Lloyd and Lyke, 1995)

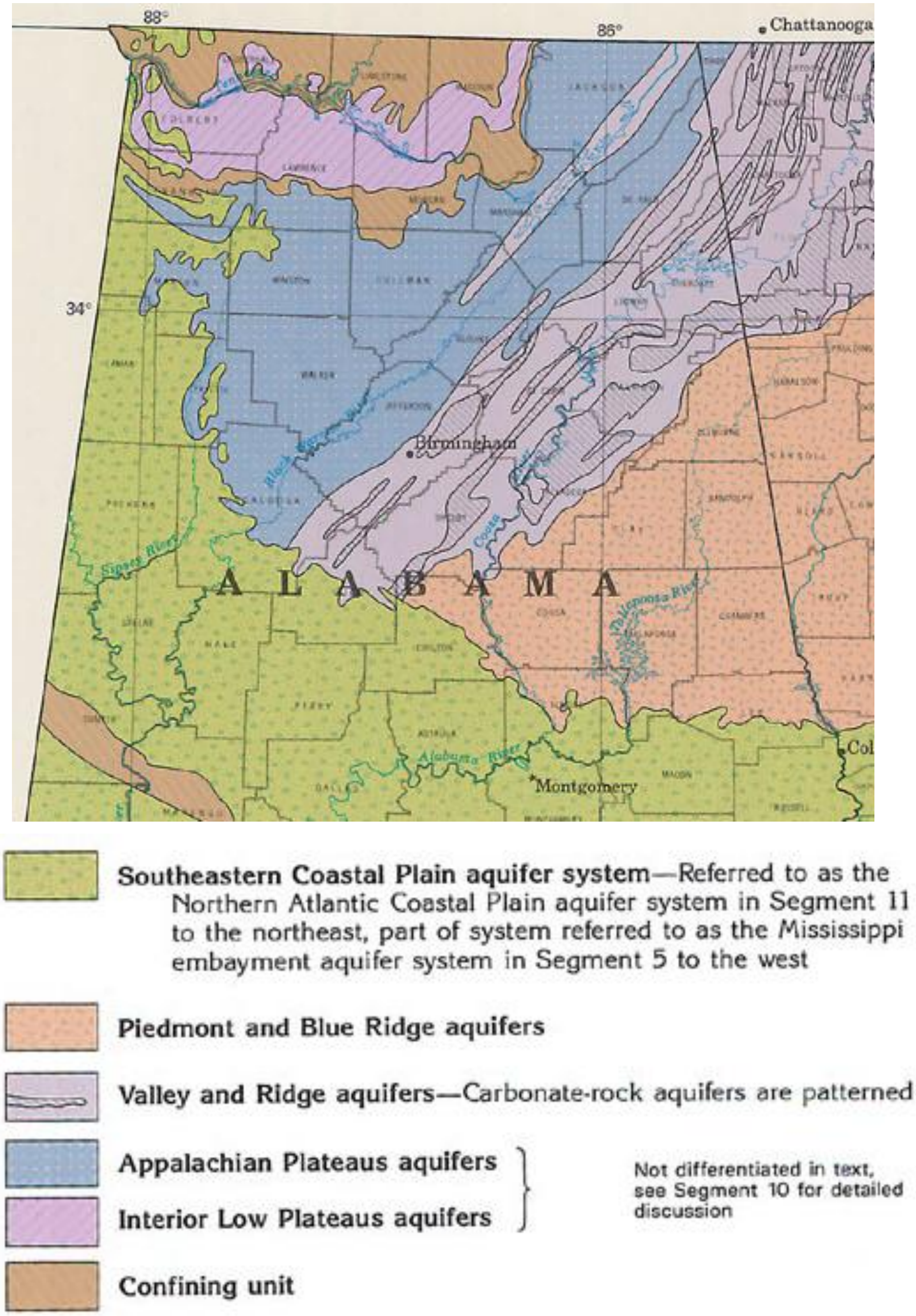
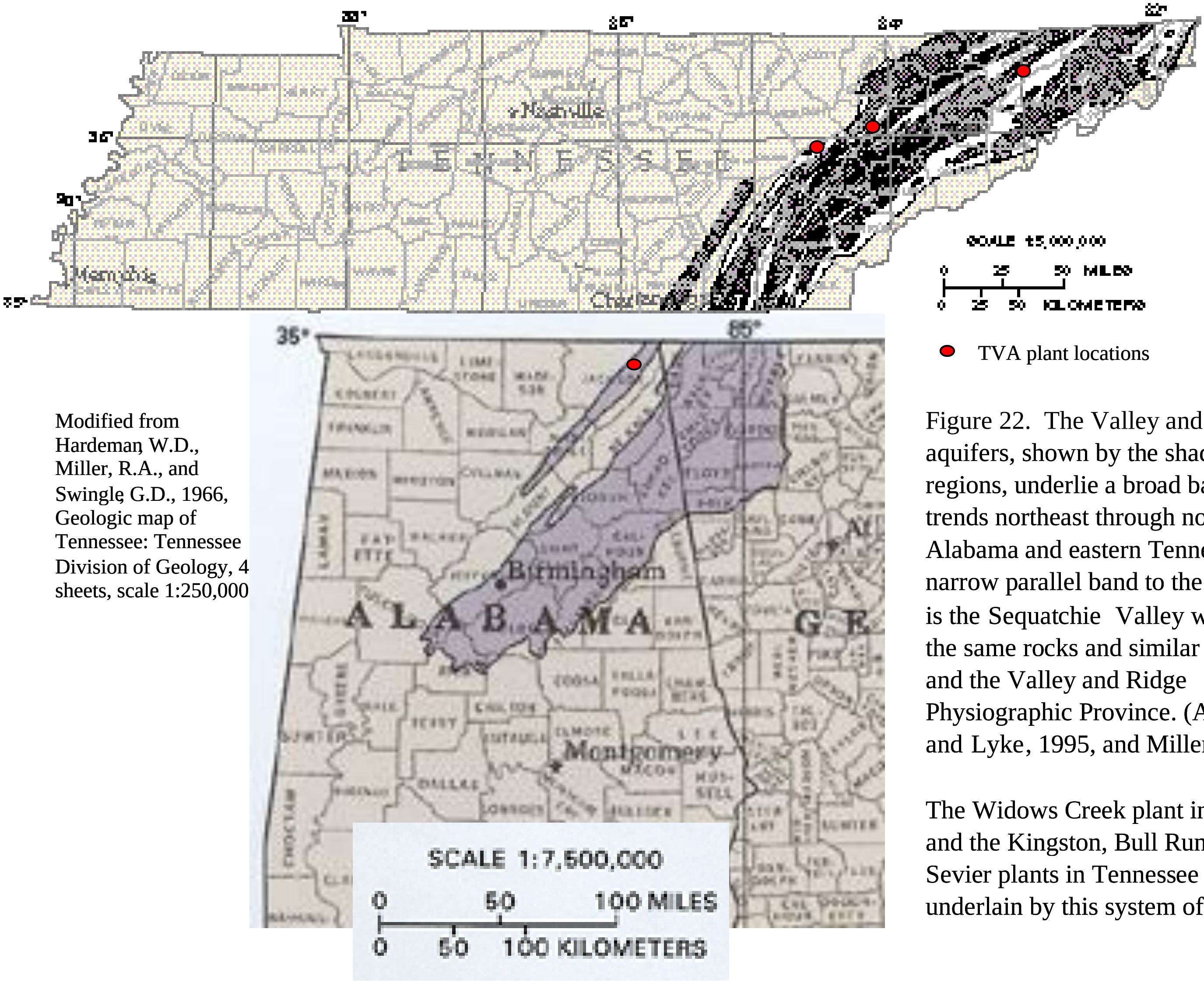


Figure 21b. Surface distribution of the major aquifer systems, continued. Segment numbers refer to regions designated in the U.S.G.S. Atlas of the U.S. (From Miller, 1990)

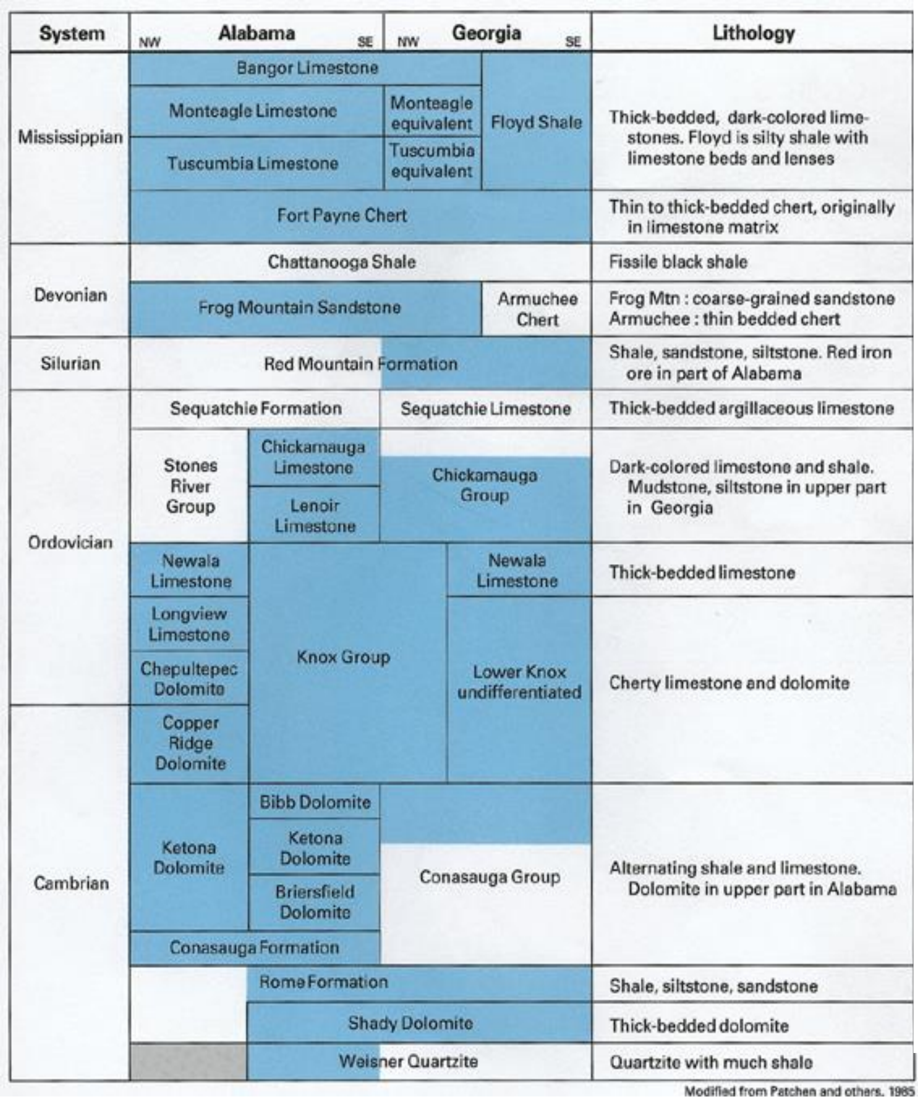


● TVA plant locations

Modified from Hardeman, W.D., Miller, R.A., and Swingle, G.D., 1966, Geologic map of Tennessee: Tennessee Division of Geology, 4 sheets, scale 1:250,000

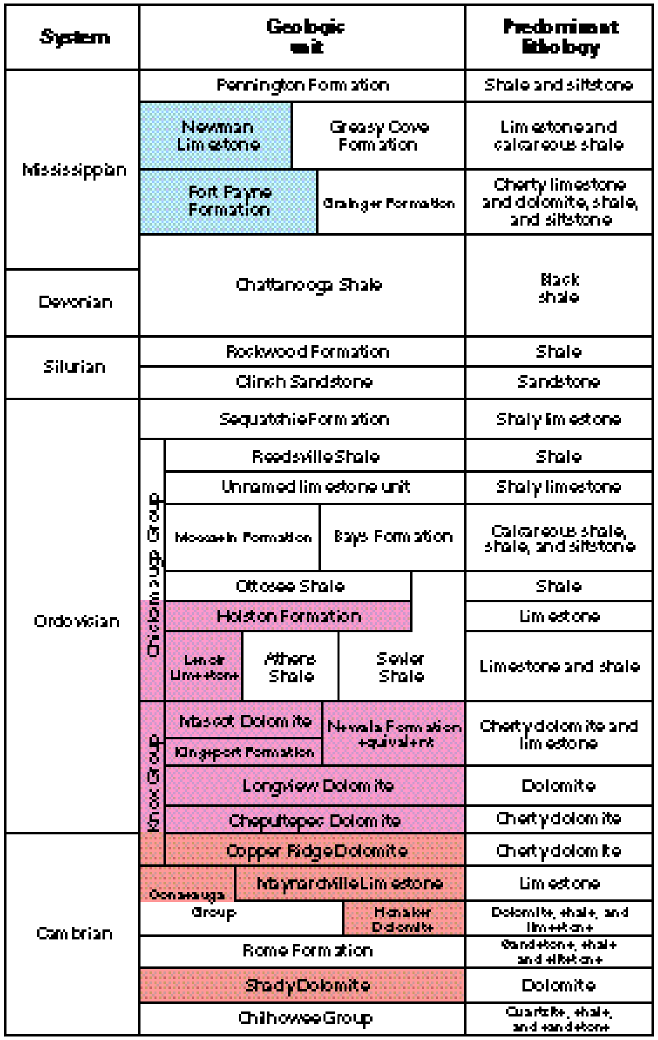
Figure 22. The Valley and Ridge aquifers, shown by the shaded regions, underlie a broad band that trends northeast through northern Alabama and eastern Tennessee. The narrow parallel band to the northwest is the Sequatchie Valley which has the same rocks and similar structures and the Valley and Ridge Physiographic Province. (After Lloyd and Lyke, 1995, and Miller, 1990)

The Widows Creek plant in Alabama and the Kingston, Bull Run, and John Sevier plants in Tennessee are underlain by this system of aquifers.



System	Alabama (NW–SE)	Georgia (NW–SE)	Lithology
Mississippian	Bangor Limestone Monteagle Limestone Tuscumbia Limestone	Monteagle equivalent Tuscumbia equivalent Floyd Shale	Thick-bedded, dark-colored limestones. Floyd is silty shale with limestone beds and lenses
	Fort Payne Chert	Fort Payne Chert	Thin to thick-bedded chert, originally in limestone matrix
Devonian	Chattanooga Shale	Chattanooga Shale	Fissile black shale
	Frog Mountain Sandstone	Armuchee Chert	Frog Mtn : coarse-grained sandstone Armuchee : thin bedded chert
Silurian	Red Mountain Formation	Red Mountain Formation	Shale, sandstone, siltstone. Red iron ore in part of Alabama
Ordovician	Sequatchie Formation	Sequatchie Limestone	Thick-bedded argillaceous limestone
	Stones River Group Chickamauga Limestone Lenoir Limestone	Chickamauga Group	Dark-colored limestone and shale. Mudstone, siltstone in upper part in Georgia
	Newala Limestone Knox Group	Newala Limestone	Thick-bedded limestone
	Longview Limestone Chepultepec Dolomite Knox Group	Lower Knox undifferentiated	Cherty limestone and dolomite
Cambrian	Copper Ridge Dolomite Knox Group	Lower Knox undifferentiated	Cherty limestone and dolomite
	Ketona Dolomite Bibb Dolomite Ketona Dolomite Brierfield Dolomite Conasauga Formation	Conasauga Group	Alternating shale and limestone. Dolomite in upper part in Alabama
	Rome Formation	Rome Formation	Shale, siltstone, sandstone
	Shady Dolomite	Shady Dolomite	Thick-bedded dolomite
	Weisner Quartzite	Weisner Quartzite	Quartzite with much shale

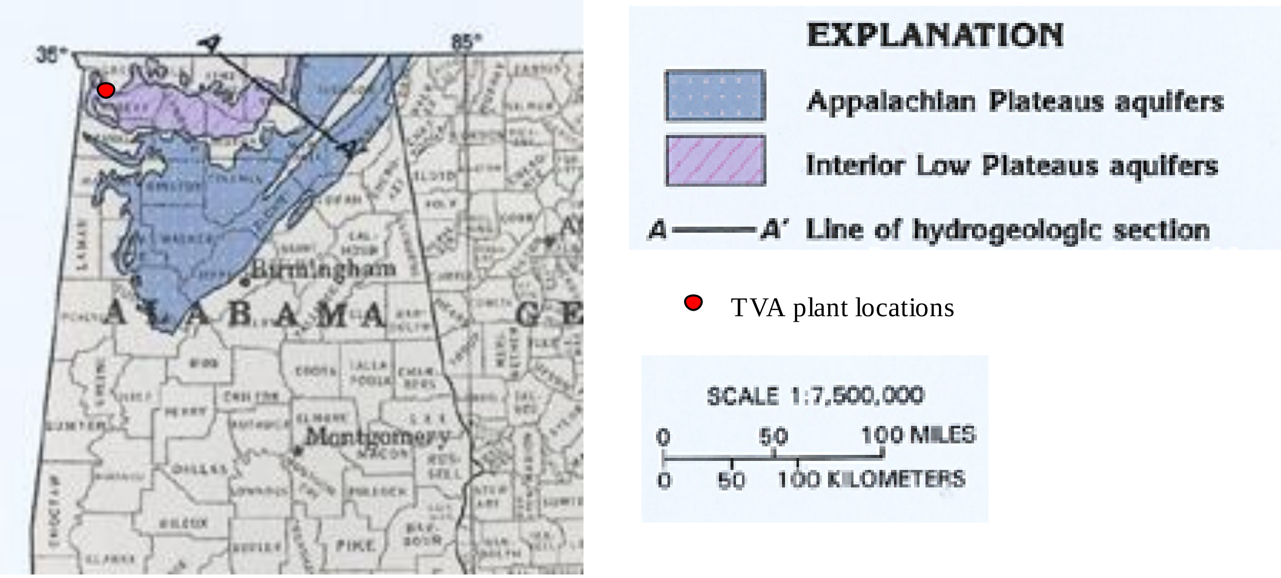
Modified from Patchen and others, 1985

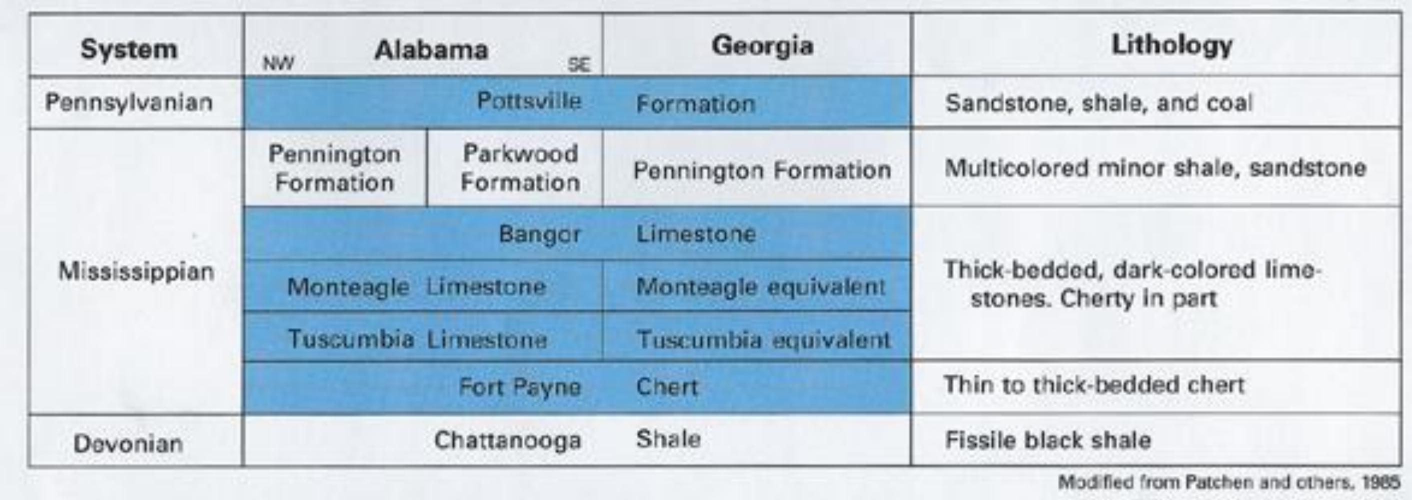


System	Geologic unit	Predominant lithology
Mississippian	Pennington Formation	Shale and siltstone
	Newman Limestone Greasy Cove Formation	Limestone and calcareous shale
	Fort Payne Formation Grainger Formation	Cherty limestone and dolomite, shale, and siltstone
Devonian	Chattanooga Shale	Black shale
Silurian	Rockwood Formation	Shale
	Clinch Sandstone	Sandstone
Ordovician	Sequatchie Formation	Shaly limestone
	Chickamauga Group: Reedsville Shale	Shale
	Chickamauga Group: Unnamed limestone unit	Shaly limestone
	Chickamauga Group: Moccasin Formation Bays Formation	Calcareous shale, shale, and siltstone
	Chickamauga Group: Ottosee Shale	Shale
	Chickamauga Group: Holston Formation	Limestone
	Chickamauga Group: Lenoir Limestone Athens Shale Sevier Shale	Limestone and shale
	Knox Group: Mascot Dolomite Kingsport Formation Newala Formation equivalent	Cherty dolomite and limestone
	Knox Group: Longview Dolomite	Dolomite
	Knox Group: Chepultepec Dolomite	Cherty dolomite
Cambrian	Knox Group: Copper Ridge Dolomite	Cherty dolomite
	Conasauga Group: Maynardville Limestone	Limestone
	Conasauga Group: Honaker Dolomite	Dolomite, shale, and limestone
	Rome Formation	Sandstone, shale and siltstone
	Shady Dolomite	Dolomite
	Chilhowee Group	Quartzite, shale, and sandstone

Modified from Hardeman, W.D., Miller, R.A., and Swingle, G.D., 1966, Geologic map of Tennessee: Tennessee Division of Geology, 4 sheets, scale 1:250,000.

Figure 23. Valley and Ridge aquifers, denoted by the shaded regions of the stratigraphic columns in Alabama (left) and Tennessee (right). All other formations are confining units except where shaded (sequence missing). (After Lloyd and Lyke, 1995, and Miller, 1990)

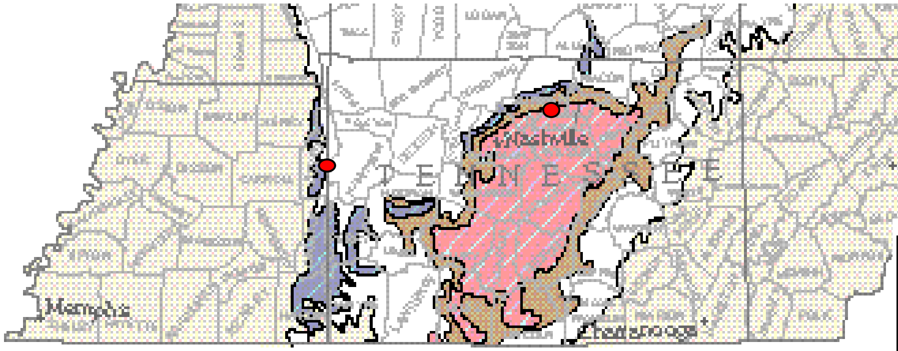




System	Alabama NW	SE	Georgia	Lithology
Pennsylvanian	Pottsville Formation			Sandstone, shale, and coal
Mississippian	Pennington Formation	Parkwood Formation	Pennington Formation	Multicolored minor shale, sandstone
	Bangor Limestone			Thick-bedded, dark-colored limestones. Cherty in part
	Monteagle Limestone		Monteagle equivalent	
	Tuscumbia Limestone		Tuscumbia equivalent	
	Fort Payne Chert			Thin to thick-bedded chert
Devonian	Chattanooga Shale			Fissile black shale

Modified from Patchen and others, 1985

Figure 24. Flat lying Paleozoic sedimentary rocks comprise the Appalachian Plateaus Interior Low Plateaus aquifer system in Alabama. The Chattanooga Shale forms the basal confining unit of the potable groundwater flow system. The most productive aquifers above the Chattanooga consist of limestone and are shown in color. The Colbert plant is underlain by this system. (After Miller, 1990)



Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1972

Modified from King, P.B., and Beikman, H.M., 1974, Geologic map of the United States: U.S. Geological Survey, 3 sheets, scale 1:2,500,000.

▨ Silurian-Devonian aquifers

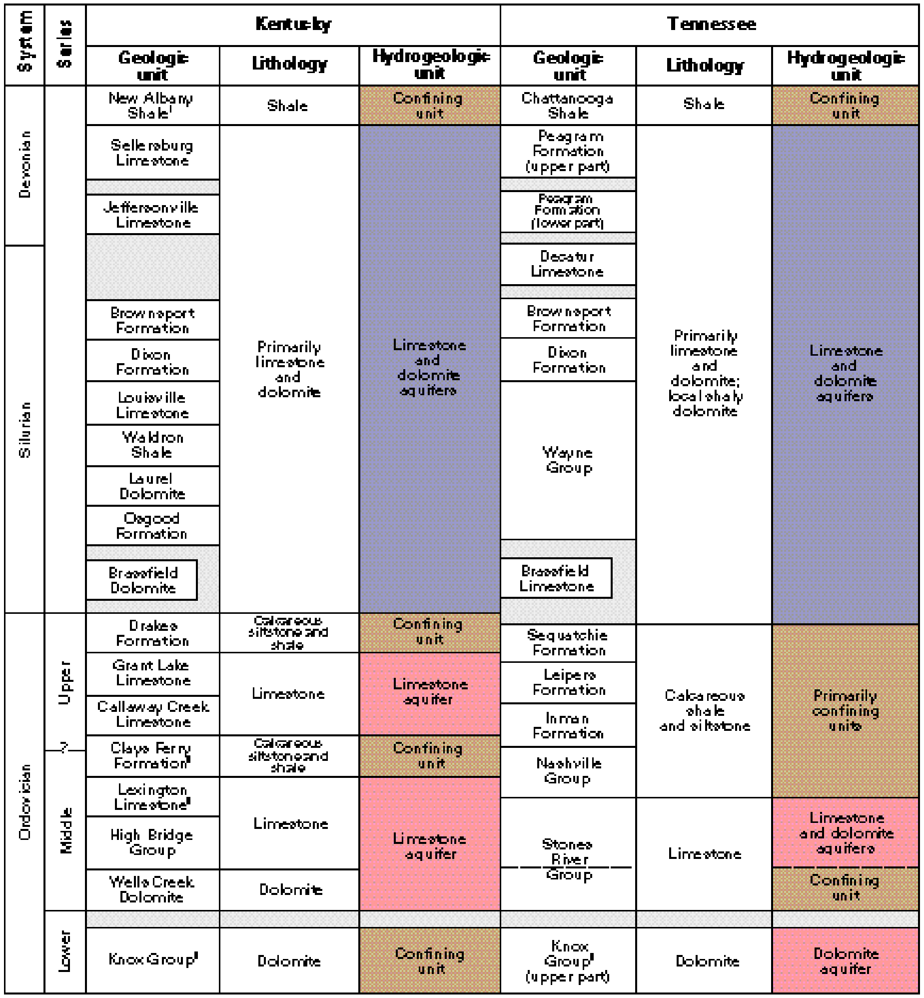
▨ Ordovician aquifers

▨ Upper Ordovician rocks

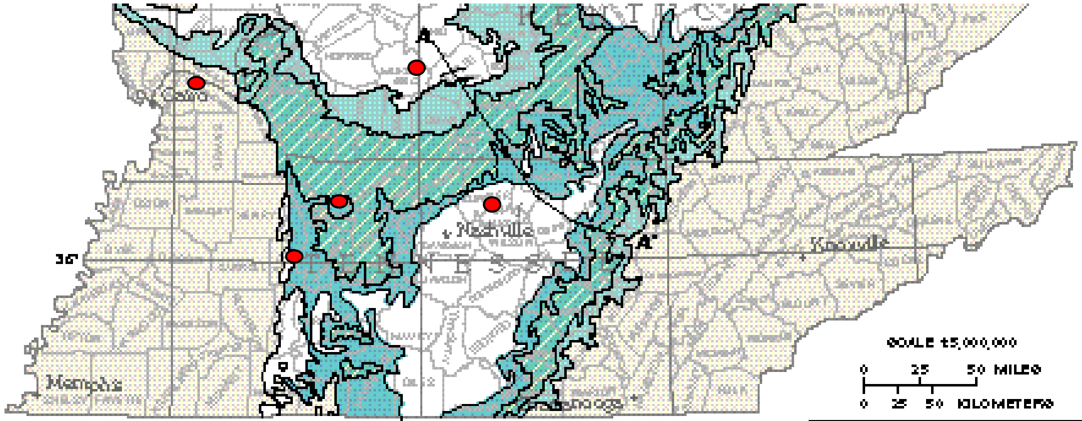
● TVA plant locations

Figure 25. Aquifers in carbonate rocks of Devonian, silurian , and Ordovicial ages underlie large parts of central Tennessee in the Interior Low Plateaus Province. Most Upper Ordovician rocks are confining units, although some locally yield small quantities of water. (After Lloyd and Lyke , 1995)

The Johnsonville and Gallatin plants in Tennessee are underlain by this system of aquifers.



System	Series	Kentucky Geologic unit	Kentucky Lithology	Kentucky Hydrogeologic unit	Tennessee Geologic unit	Tennessee Lithology	Tennessee Hydrogeologic unit
Devonian		New Albany Shale¹	Shale	Confining unit	Chattanooga Shale	Shale	Confining unit
		Sellersburg Limestone	Primarily limestone and dolomite	Limestone and dolomite aquifers	Peagram Formation (upper part)	Primarily limestone and dolomite; local shaly dolomite	Limestone and dolomite aquifers
		Jeffersonville Limestone			Peagram Formation (lower part)		
Silurian					Decatur Limestone		
		Brownsport Formation			Brownsport Formation		
		Dixon Formation			Dixon Formation		
		Louisville Limestone			Wayne Group		
		Waldron Shale					
		Laurel Dolomite					
		Osgood Formation					
		Brassfield Dolomite			Brassfield Limestone		
Ordovician	Upper	Drakes Formation	Calcareous siltstone and shale	Confining unit	Sequatchie Formation	Calcareous shale and siltstone	Primarily confining units
		Grant Lake Limestone	Limestone	Limestone aquifer	Leipers Formation		
		Callaway Creek Limestone			Inman Formation		
	?	Clays Ferry Formation¹	Calcareous siltstone and shale	Confining unit	Nashville Group		
	Middle	Lexington Limestone¹	Limestone	Limestone aquifer	Stones River Group	Limestone	Limestone and dolomite aquifers
		High Bridge Group					
		Wells Creek Dolomite	Dolomite				Confining unit
	Lower	Knox Group¹	Dolomite	Confining unit	Knox Group¹ (upper part)	Dolomite	Dolomite aquifer



EXPLANATION

▨ **Mississippian aquifers**

▨ **Upper Mississippian rocks**—Generally confining units but may contain local aquifers

▨ **Lower Mississippian rocks**—Generally confining units but may contain local aquifers

— **Fault**

—A' **Line of hydrogeologic section**

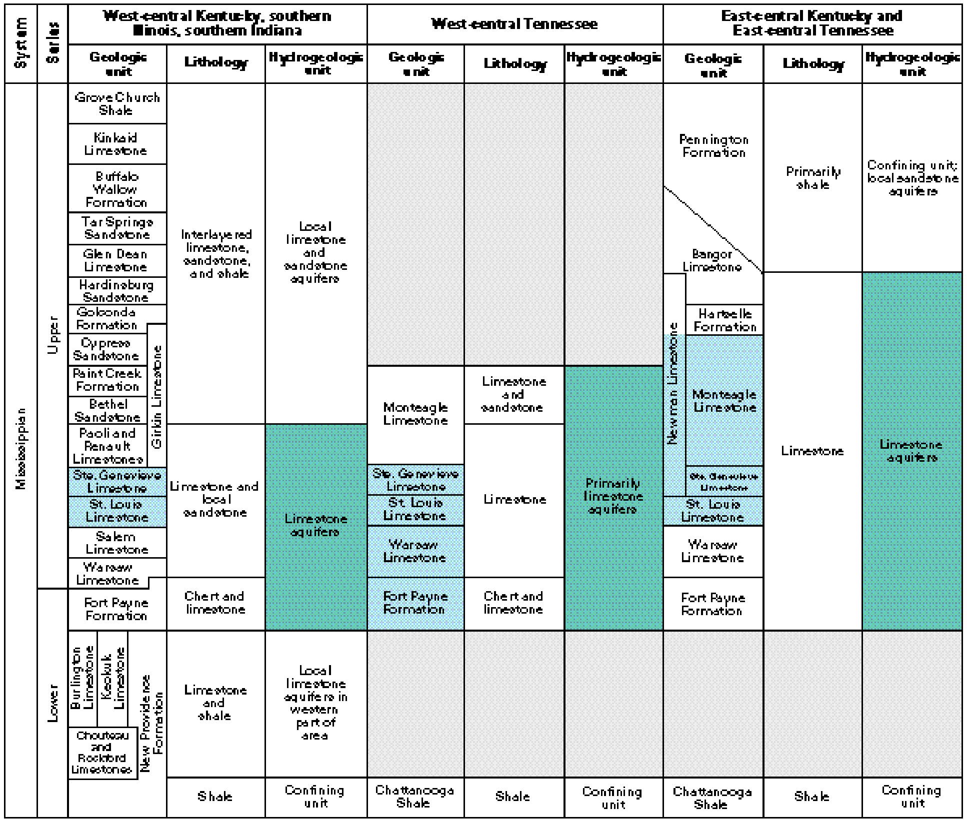
● TVA plant locations

Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1972

Modified from King, P.B., and Beikman, H.M., 1974, Geologic map of the United States: U.S. Geological Survey, 3 sheets, scale 1:2,500,000.

Figure 26. Rocks of Mississippian age underlie a large part of the Interior Low Plateaus Province. The principal aquifers in these rocks are primarily Upper Mississippian limestones. The most productive aquifers in this system are the Ste. Genevieve, the St. Louis, and the Warsaw Limestones , and the Fort Payne Formation. These are shown shaded in blue. (After Lloyd and Lyke, 1995)

The Jacksonville and Cumberland plants in Tennessee are underlain by this aquifer system. Plants that are in close proximity include the Gallatin plant in Tennessee and the Shawnee and Paradise plants in Kentucky.



System	Series	West-central Kentucky, southern Illinois, southern Indiana			West-central Tennessee			East-central Kentucky and East-central Tennessee		
		Geologic unit	Lithology	Hydrogeologic unit	Geologic unit	Lithology	Hydrogeologic unit	Geologic unit	Lithology	Hydrogeologic unit
Mississippian	Upper	Grove Church Shale	Interlayered limestone, sandstone, and shale	Local limestone and sandstone aquifers				Pennington Formation	Primarily shale	Confining unit; local sandstone aquifers
		Kinkaid Limestone								
		Buffalo Wallow Formation								
		Tar Springs Sandstone								
		Glen Dean Limestone						Bangor Limestone		
		Hardinsburg Sandstone						Newman Limestone	Limestone	Limestone aquifers
		Golconda Formation						Hartselle Formation		
		Girkin Limestone: Cypress Sandstone						Monteagle Limestone		
		Girkin Limestone: Paint Creek Formation			Monteagle Limestone	Limestone and sandstone	Primarily limestone aquifers			
		Girkin Limestone: Bethel Sandstone								
		Girkin Limestone: Paoli and Renault Limestones	Limestone and local sandstone	Limestone aquifers		Limestone				
		Ste. Genevieve Limestone			Ste. Genevieve Limestone			Ste. Genevieve Limestone		
		St. Louis Limestone			St. Louis Limestone			St. Louis Limestone		
		Salem Limestone			Warsaw Limestone			Warsaw Limestone		
		Warsaw Limestone								
	Lower	Fort Payne Formation	Chert and limestone		Fort Payne Formation	Chert and limestone		Fort Payne Formation		
		Burlington Limestone Keokuk Limestone New Providence Formation	Limestone and shale	Local limestone aquifers in western part of area						
		Chouteau and Rockford Limestones								
			Shale	Confining unit	Chattanooga Shale	Shale	Confining unit	Chattanooga Shale	Shale	Confining unit

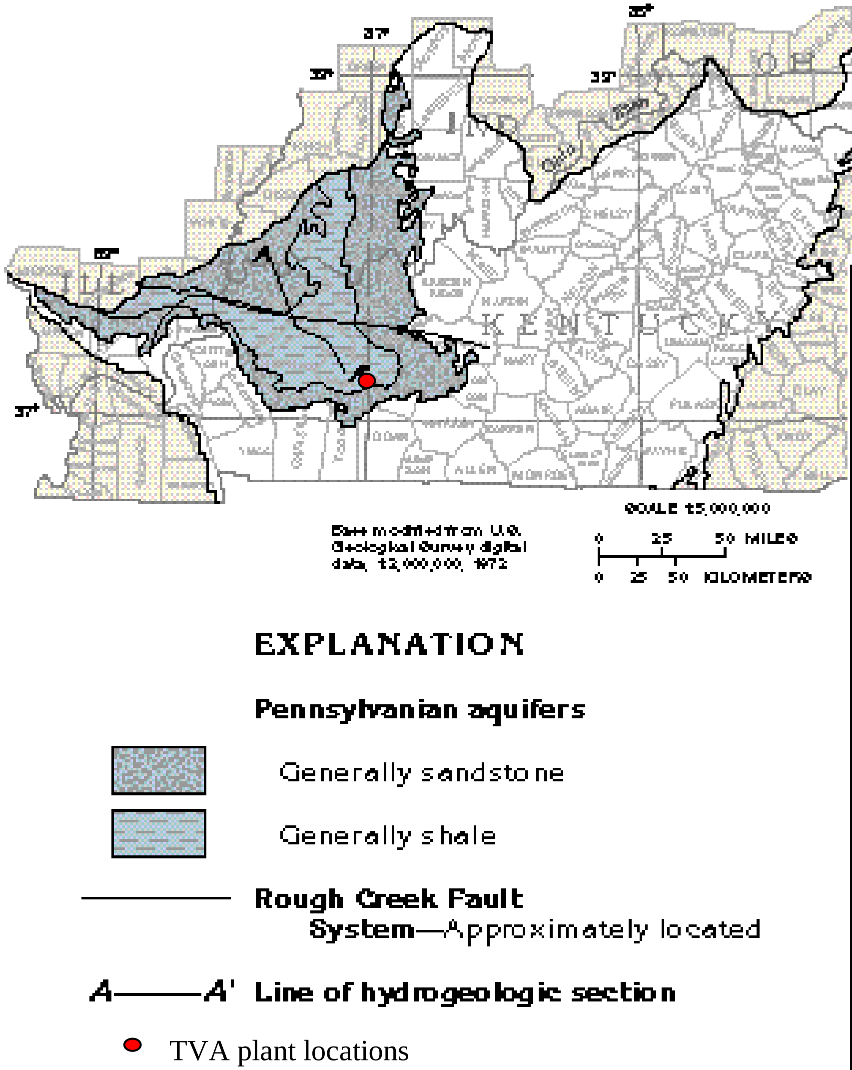
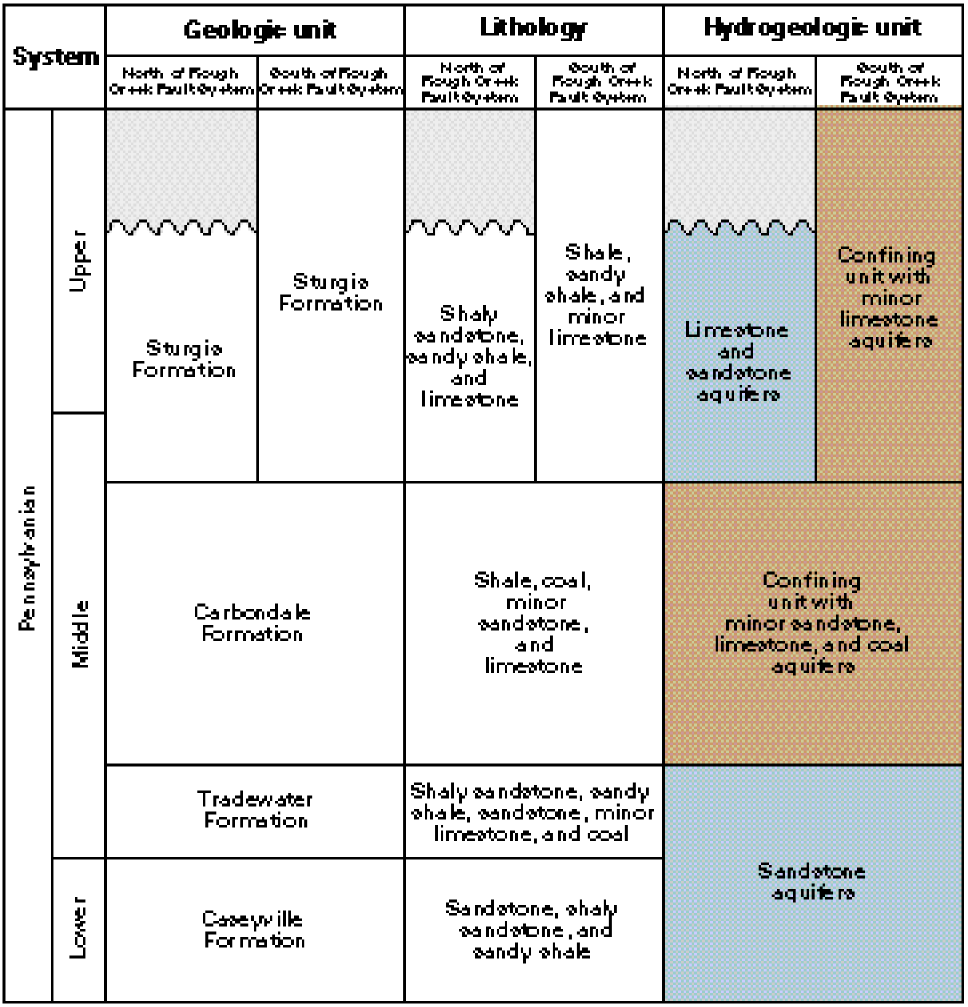
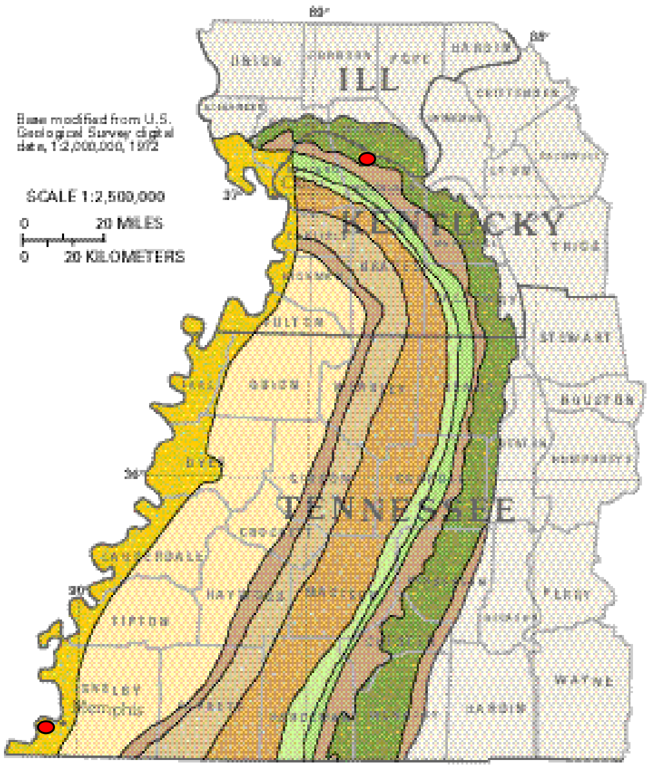


Figure 27. Sandstones that form the principal aquifers in the Pennsylvanian rocks underlie northwestern Kentucky. Most of these aquifers are in the Caseyville and the Tradewater Formations south of the Rough Creek Fault System and in the Sturgis Formation north of the fault system. (After Lloyd and Lyke, 1995)



System		Geologic unit		Lithology		Hydrogeologic unit	
		North of Rough Creek Fault System	South of Rough Creek Fault System	North of Rough Creek Fault System	South of Rough Creek Fault System	North of Rough Creek Fault System	South of Rough Creek Fault System
Pennsylvanian	Upper	Sturgis Formation	Sturgis Formation	Shaly sandstone, sandy shale, and limestone	Shale, sandy shale, and minor limestone	Limestone and sandstone aquifers	Confining unit with minor limestone aquifers
	Middle	Carbondale Formation		Shale, coal, minor sandstone, and limestone		Confining unit with minor sandstone, limestone, and coal aquifers	
		Tradewater Formation		Shaly sandstone, sandy shale, sandstone, minor limestone, and coal		Sandstone aquifers	
	Lower	Caseyville Formation		Sandstone, shaly sandstone, and sandy shale			

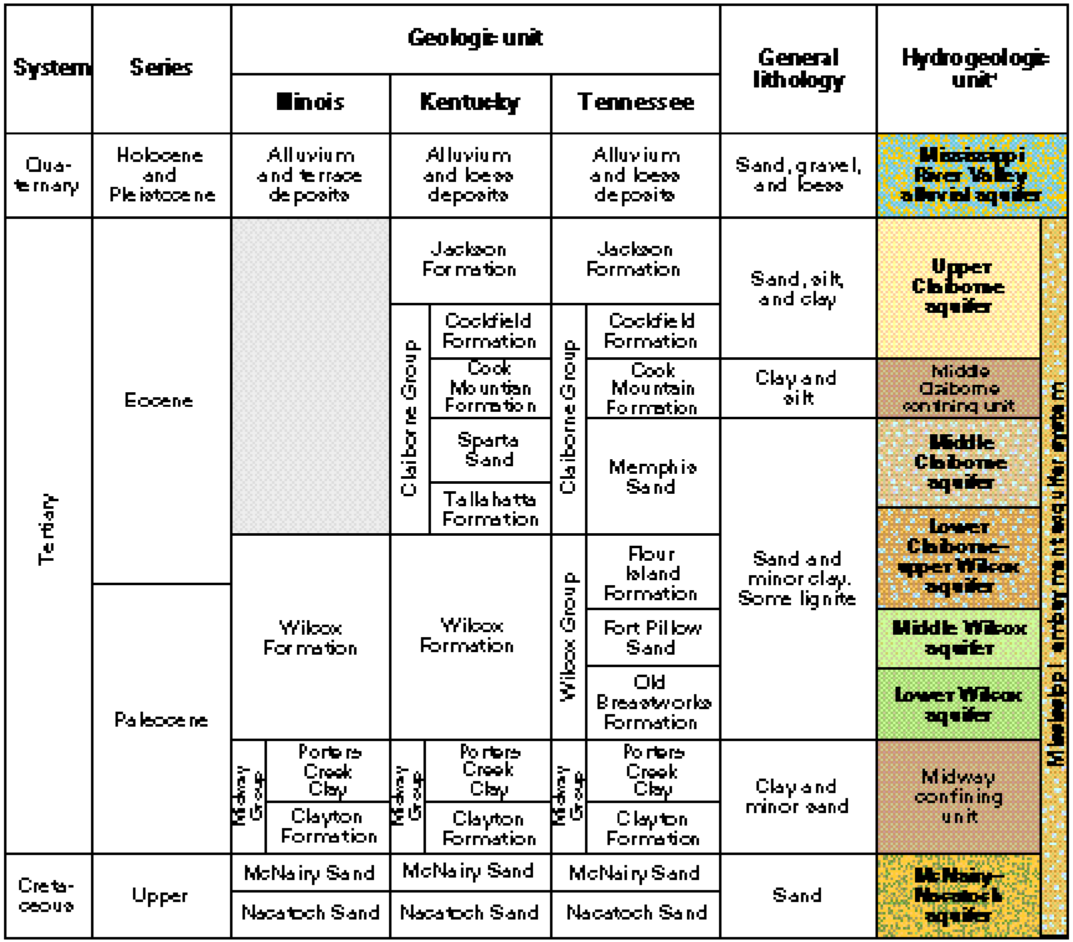
The Paradise plant in Kentucky is underlain by this system of aquifers.



Modified from Williamson, A.K., Grubb, H.F., and Weiss, J.S., 1990, Ground-water flow in the Gulf Coast aquifer systems, south-central United States—A preliminary analysis: U.S. Geological Survey Water-Resources Investigations Report 9-4071, 123 p.

Figure 28. The aquifers and confining units of the Mississippi Embayment aquifer system crop out in a sequence of arcuate bands in westernmost Kentucky and Tennessee. The aquifers are exposed on the east flank of the Mississippi Embayment, which is a large structural downward in the Coastal Plain Physiographic Province. (From Lloyd and Lyke, 1995)

The Shawnee plant in Kentucky and the Allen plant in Tennessee are underlain by this aquifer system.



System	Series	Geologic unit: Illinois		Geologic unit: Kentucky		Geologic unit: Tennessee		General lithology	Hydrogeologic unit[1]	
Quaternary	Holocene and Pleistocene		Alluvium and terrace deposits		Alluvium and loess deposits		Alluvium and loess deposits	Sand, gravel, and loess	Mississippi River Valley alluvial aquifer	
Tertiary	Eocene				Jackson Formation		Jackson Formation	Sand, silt, and clay	Upper Claiborne aquifer	Mississippi embayment aquifer system
				Claiborne Group	Cockfield Formation	Claiborne Group	Cockfield Formation			
					Cook Mountain Formation		Cook Mountain Formation	Clay and silt	Middle Claiborne confining unit	
					Sparta Sand		Memphis Sand	Sand and minor clay. Some lignite	Middle Claiborne aquifer	
					Tallahatta Formation				Lower Claiborne–upper Wilcox aquifer	
	Paleocene		Wilcox Formation		Wilcox Formation	Wilcox Group	Flour Island Formation			
							Fort Pillow Sand		Middle Wilcox aquifer	
							Old Breastworks Formation		Lower Wilcox aquifer	
		Midway Group	Porters Creek Clay	Midway Group	Porters Creek Clay	Midway Group	Porters Creek Clay	Clay and minor sand	Midway confining unit	
			Clayton Formation		Clayton Formation		Clayton Formation			
Cretaceous	Upper		McNairy Sand		McNairy Sand		McNairy Sand	Sand	McNairy–Nacatoch aquifer	
			Nacatoch Sand		Nacatoch Sand		Nacatoch Sand			

[1] Hydrogeologic unit names apply to the entire Mississippi embayment aquifer system. Local names may differ.

🟨 **Mississippi River Valley alluvial aquifer**

Mississippi embayment aquifer system

▨ Upper Claiborne aquifer

▨ Middle Claiborne aquifer

▨ Lower Claiborne–upper Wilcox aquifer

● TVA plant locations

🟩 Middle Wilcox aquifer

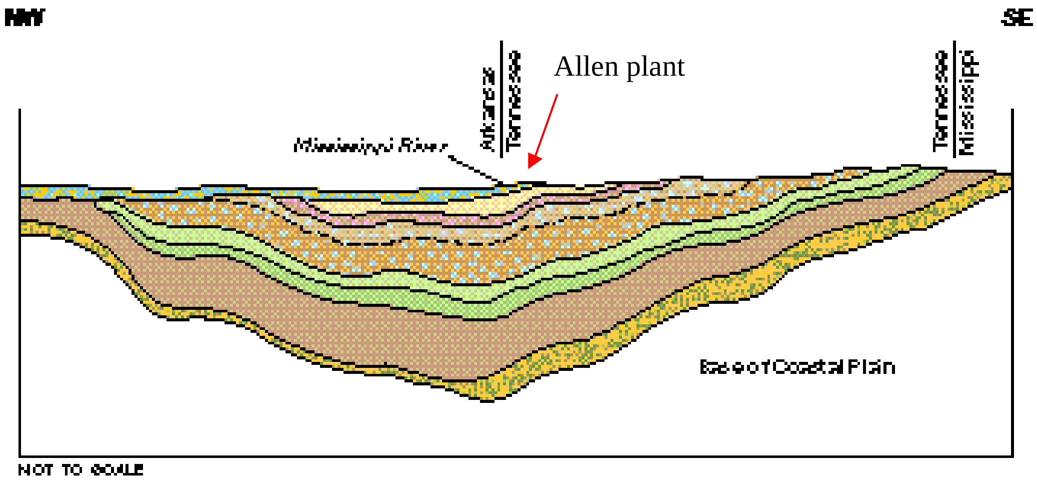
🟩 Lower Wilcox aquifer

🟩 McNairy–Nacatoch aquifer

🟫 **Confining unit**

— **Mississippi Embayment Province boundary**

— **Line of hydrogeologic section**



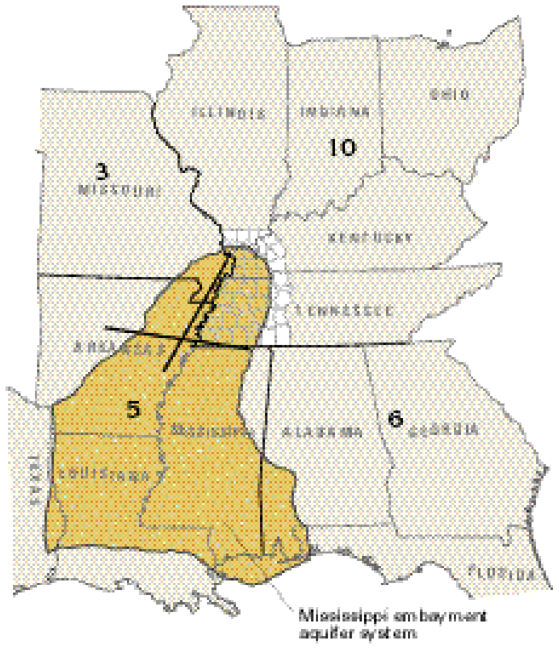
Modified from Williamson, A.K., Grubb, H.F., and Weiss, J.S., 1990, Ground-water flow in the Gulf Coast aquifer systems, south-central United States—A preliminary analysis: U.S. Geological Survey Water-Resources Investigations Report 9–4071, 123 p.

▨ **Mississippi River Valley alluvial aquifer**

Mississippi embayment aquifer system

- ▨ Upper Claiborne aquifer
- ▨ Middle Claiborne confining unit
- ▨ Middle Claiborne aquifer
- ▨ Lower Claiborne–upper Wilcox aquifer
- ▨ Middle Wilcox aquifer
- ▨ Lower Wilcox aquifer
- ▨ Midway confining unit
- ▨ McNairy-Nacatoch aquifer

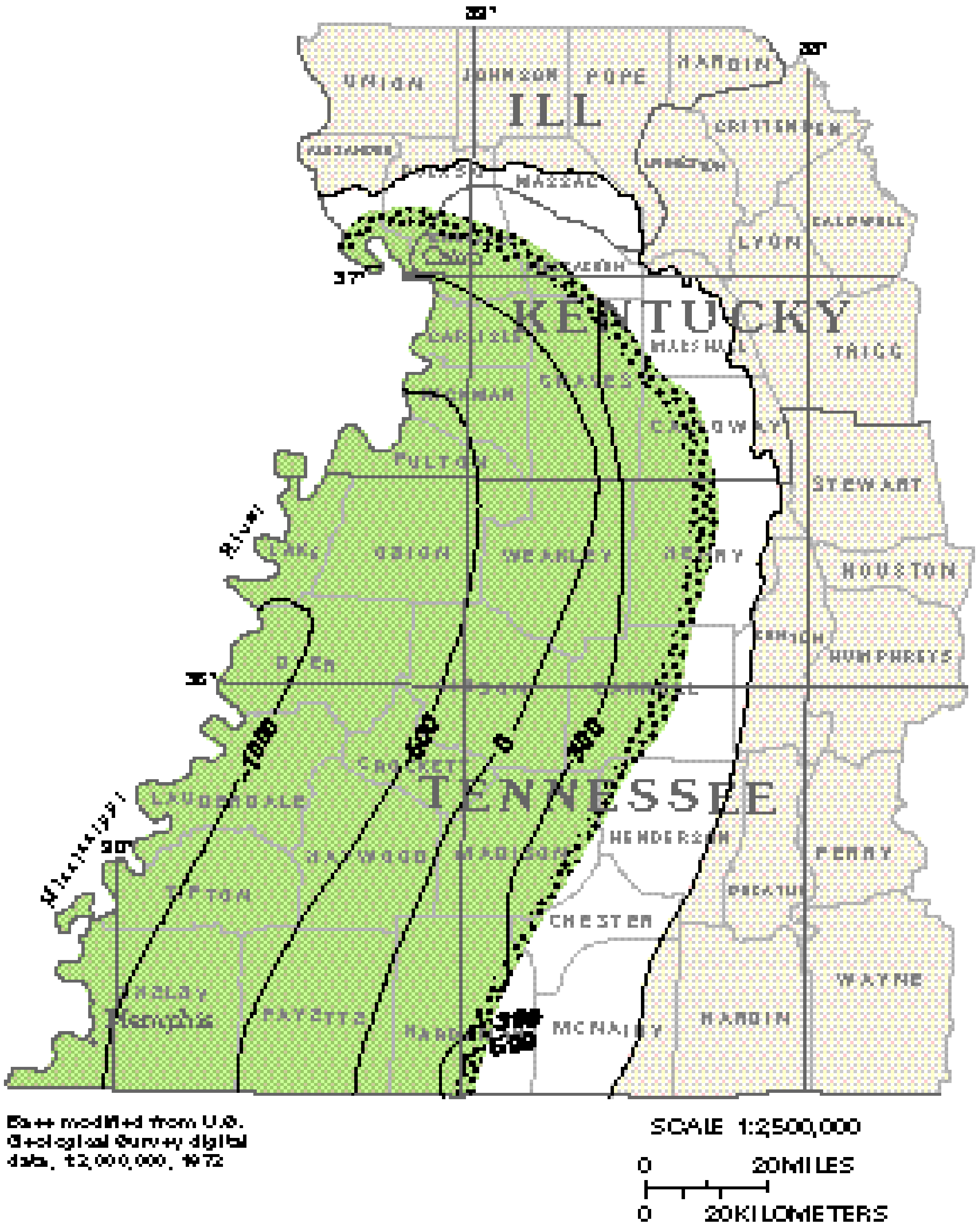
———---- **Hydrogeologic unit boundary** —Dashed where approximately located



Modified from Hosman, R.L., and Weiss, J.S., 1991, Geohydrologic units of the Mississippi embayment and Texas Coastal Uplands aquifer systems, south-central United States: U.S. Geological Survey Professional Paper 1416–B, 19 p.

Figure 29. The Mississippi Embayment aquifer system in Kentucky and Tennessee thickens toward the west; the thickest part underlies the Mississippi River. The aquifers in rocks of Cretaceous and Tertiary age are exposed at land surface in most of Tennessee but are covered by Quaternary sediments that compose the Mississippi River Valley alluvial aquifer in westernmost Tennessee. The approximate location of this generalized section is shown above. (After Lloyd and Lyke, 1995)

The Allen plant in Tennessee (indicated on the cross section) and the Shawnee plant in Kentucky are underlain by this aquifer system.



Modified from Hosman, R.L., and Weiss, J.S., 1991, Geohydrologic units of the Mississippi embayment and Texas Coastal Uplands aquifer systems, south-central United States: U.S. Geological Survey Professional Paper 1416-B, 19 p.

Figure 30. The altitude of the top of the lower Wilcox aquifer is about 500 feet above sea level where the aquifer crops out in Tenn. The top slopes downward to more that 1,000 feet below sea level near the axis of the Mississippi Embayment along the Mississippi River.

The Allen and Shawnee plants are underlain by this aquifer, as indicated. (After Lloyd and stream prior to transport. This is true in eastern Tennessee, for example, where successful production of the Swan Creek gas field has led to the speculation that other similar fields may exist within the heavily faulted Valley and Ridge Province (Hatcher et al., 2001). Gas from that field contains no sulfur, no CO_2, and very little nitrogen, requiring only minor processing to remove water and condensate prior to shipping it to markets via pipelines.

The availability of data regarding the distribution of oil, gas, and coal fields is mixed. The Kentucky Geological Survey has provided information on their website (www.uky.edu/KGS) showing the distribution of oil and gas producing wells (Figure 31) and resource estimates for the Springfield Coal bed in northwestern Kentucky (Figure 32). This type of consolidated information is more difficult to locate for sites in Tennessee and Alabama, however. The Tennessee Division of Geology maintains a listing of deep test wells in the state as well as borehole logs and other information provided by the drillers. The information is not complete, however, and it requires a trip to the Nashville offices to personally sift through the borehole records.

Luther (1959) describes the distribution and reserves of the Tennessee coalfield, underlying the Cumberland Plateau from northeastern Alabama across east Tennessee and into eastern Kentucky. However, the Pennsylvanian strata containing the coal beds are truncated by a series of thrust faults that make up the boundary between the Cumberland Plateau and the Valley and Ridge physiographic units. The Sequatchie Valley is also excluded from this distribution, presumably a result of similar erosional loss of the Pennsylvanian strata due to thrust faulting. Thus the major coal-producing region in Tennessee is not in close proximity to any of the TVA plants included in this study.

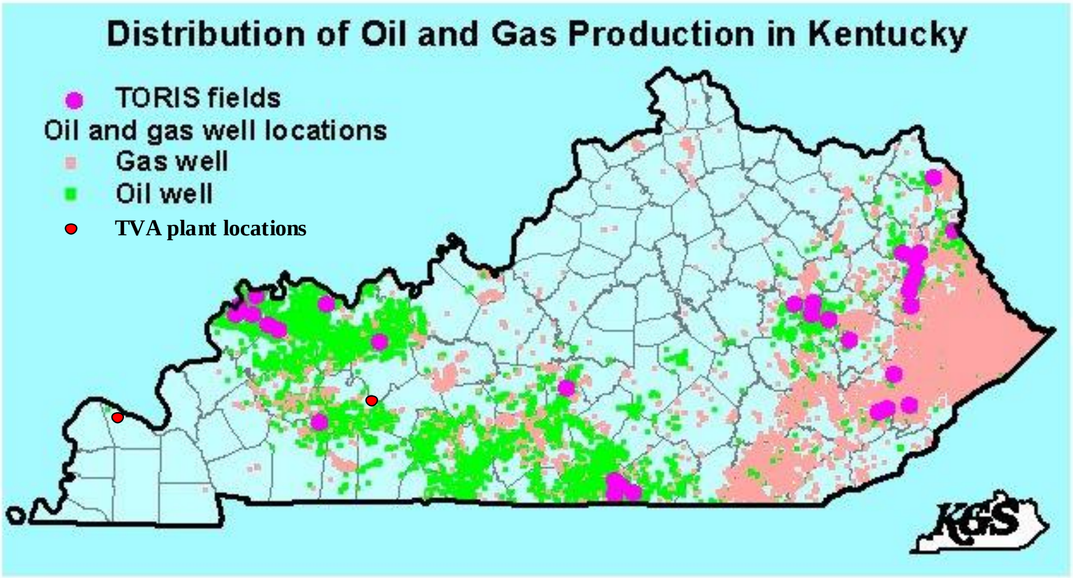


Figure 31. Distribution of oil and gas production in Kentucky. The Paradise and Shawnee plant locations are shown. The Tertiary Oil Recovery Information System (TORIS) is a public database maintained by the National Petroleum Council and used by the U.S. Department of Energy for assessing domestic oil reserves. (From www.uky.edu/KGS)

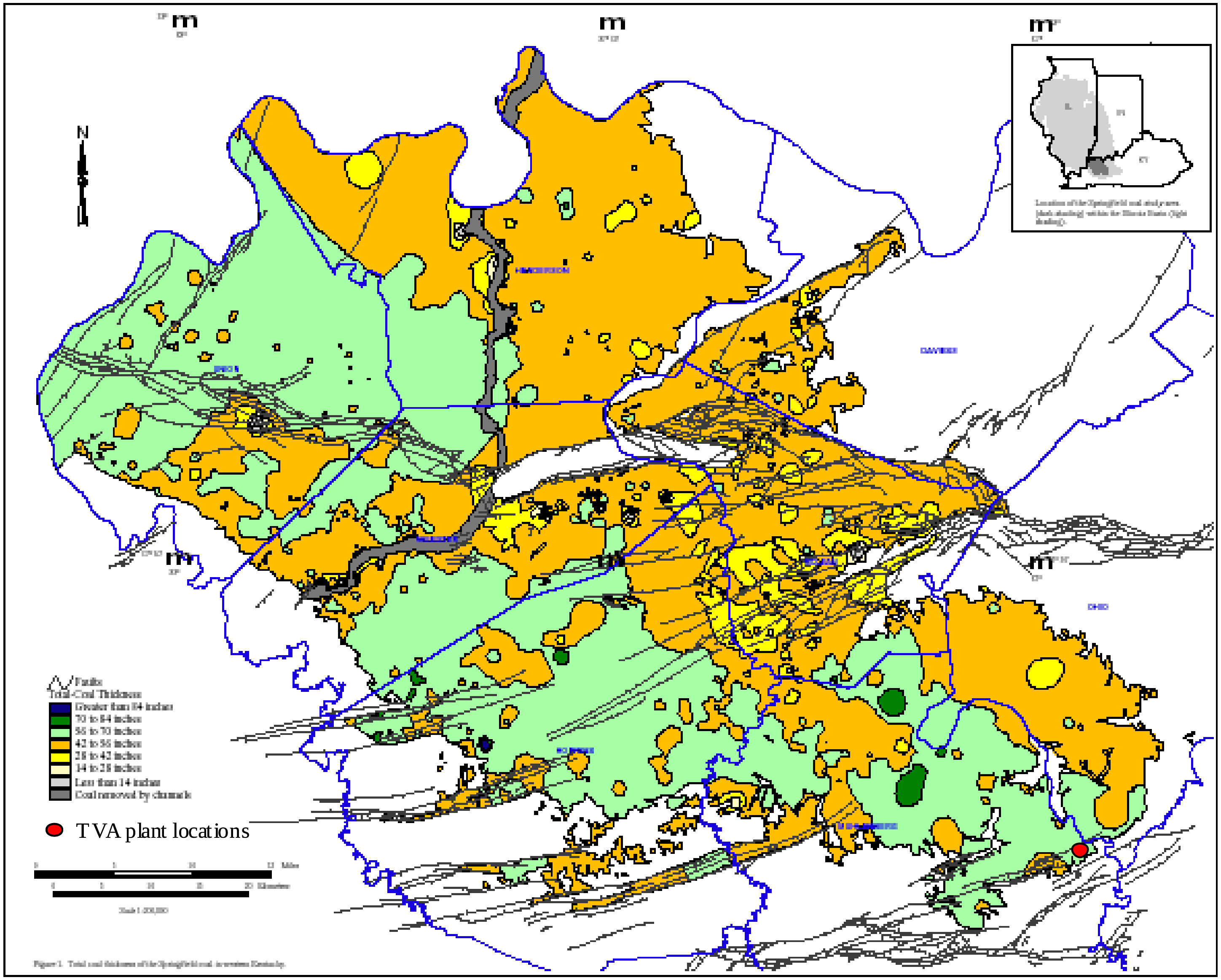


Figure 32. Resource estimates and distribution of the Springfield Coal in Kentucky. The map area is represented by the dark shading in the inset. The red circle in the SE corner of the map is the Paradise plant location. (From Andrews et al., 2000)

A review of the summary of deep tests in Tennessee (State of TN, Division of Geology) shows that of the 63 wells listed all but 6 are classified as either dry and abandoned or as waste disposal wells. This listing does not appear to include wells from the Swan Creek field in Hancock Co., Tennessee (Hatcher et al., 2001). However many of the well reports indicate gas or oil shows, most commonly within the Ordovician rocks but also some in the Mississippian strata. The Swan Creek field is producing both oil and gas from the Middle Ordovician Stones River Group, and from the Upper Cambrian-Lower Ordovician Knox Group, respectively (Figure 33). These formations and their stratigraphic equivalents appear to be the primary hydrocarbon-producing rocks across the state based on the reported shows. Six of the seven TVA fossil plants in Tennessee have at least one deep test well located close enough to the plant location to be useful in grossly estimating the depth to key formations and in some cases the thickness of potentially porous rocks.

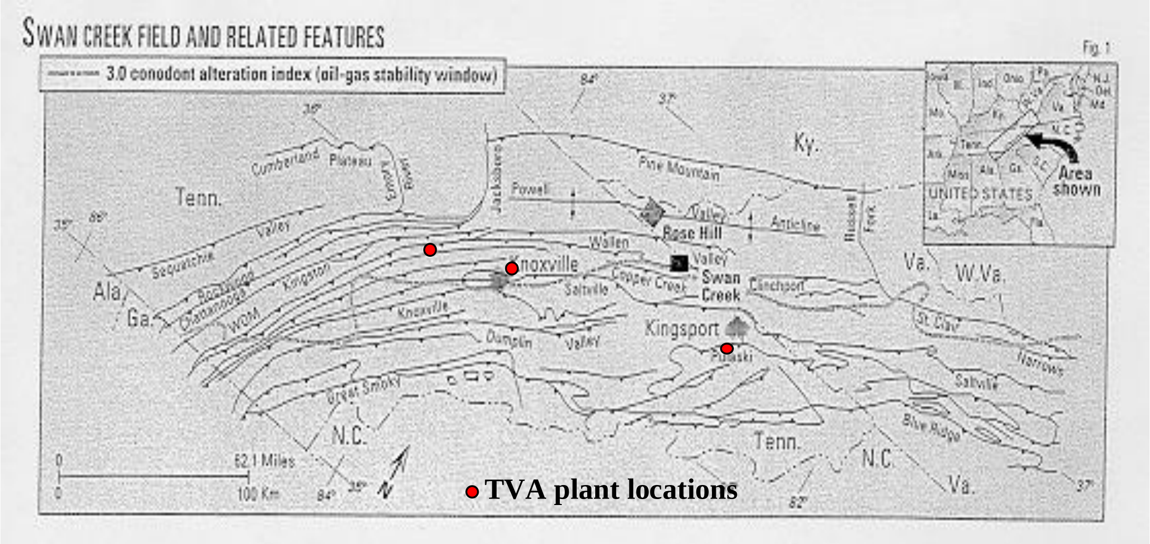
Least well known is information on hydrocarbon resources for the sites in northern Alabama. Many of the publications offered through the Geological Survey of Alabama are out of print. GSA maintains an interactive website that allows access to maps of the bedrock geology and recharge areas for major aquifers. However the oil and gas maps are not yet available online. A query of the database of wells, searchable by county, listed no penetrations in Colbert County and only three in Jackson County. The total depth of those wells was fairly shallow, ranging from 1875-3935 feet. No other information, such as the target interval or eventual outcome of the well was provided.

Depths to the 32º C isotherm and 7.4 MPa isobar

Figure 34 shows a phase diagram for CO_2, in which it can be seen that the minimum temperature and pressure at which supercritical conditions are met are 32ºC and 7.4 MPa, respectively (Bachu, 2000). While CO_2 can be injected in any of the phases indicated, the supercritical phase is preferable because the physical characteristics and behavior at these conditions provide the most efficient use of reservoir storage capacity. There is an economic tradeoff between injection at supercritical depths and the additional cost of drilling at greater depths. Thus, the practical upper limit for the depth to injection target will be governed primarily by economics and the sequestration potential of a deeper target.

Previous studies have assumed implicitly that the pressure distribution in a sedimentary basin is hydrostatic, increasing linearly with depth at the rate of 1 MPa per 100 m (e.g., Holloway and Savage, 1993; van der Meer, 1993). These studies further assumed an average geothermal gradient of 25ºC/km, to arrive at a minimum depth of 800 m for the conditions at which CO_2 would be in a supercritical state. In the absence of other data, these average gradients provide a reasonable rule of thumb for determining a minimum injection depth.

Several conditions can alter this depth estimate, however. First, the depth to the 32ºC isotherm is dependent on the average surface temperature for the region of interest. Second, the average geothermal gradient assumes a hydrostatic condition which is often not the case in deep aquifer systems. Most regional flow systems in continental basins are driven by topography from recharge areas at high elevations to discharge areas at low elevations. The movement of formation water carries heat, often at much faster rates than simple convection. Thus the 32ºC isotherm may be found at greater depths beneath recharge areas and shallower depths beneath discharge areas. Finally, the hydrostatic pressure gradient may not represent actual subsurface pressures if the system is, in fact, hydrostatic due to compartmentalization. This occurs when stratigraphic or structural features completely isolate a subsurface region from neighboring regions. Hydrocarbon production, uplift and erosion, and burial can all create conditions in which pressures are not at equilibrium because flow is restricted (AAPG, 1994).



For the purposes of this study, the following assumptions will be made: (1) regional flow is topographically-driven, (2) ambient flow rates are low enough to assume the average hydrostatic and geothermal gradients, and (3) the average surface temperature is 14ºC, based on average temperatures ranging between 55-60ºF across the study region for the years 1961-1990 (NOAA). Using these assumptions, the depth to the 32ºC isotherm is 720 m and the depth to the 7.4 MPa isobar is 740 m. Adding some margin of safety for hydrodynamic effects, a minimum depth of 2500 ft (762 m) was assumed.

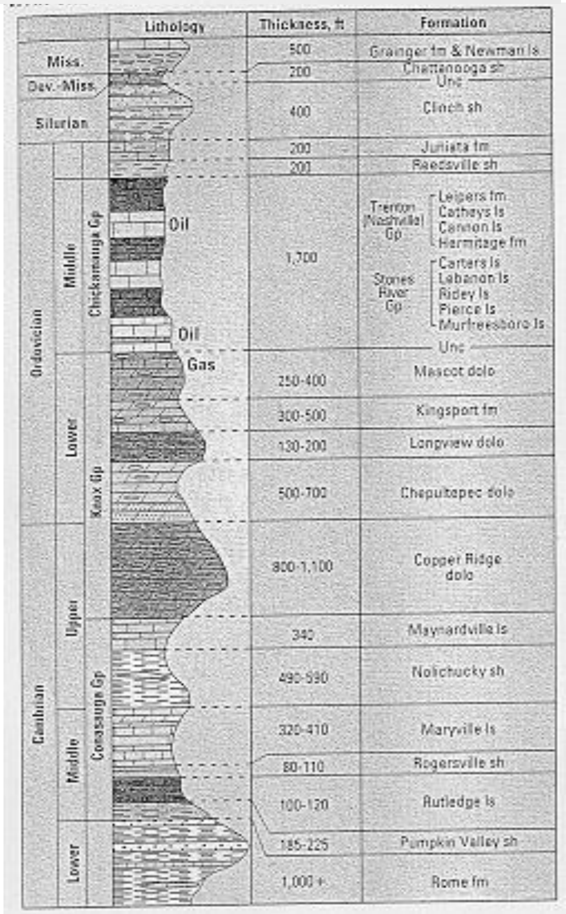


Figure 33. The Swan Creek gas field in the Valley and Ridge Province in eastern Tennessee. The older Rose Hill field is also shown. The approximate locations of the John Sevier, Bull Run, and Kingsport plants are indicated by the red circles from right to left, respectively. (From Hatcher et al., 2001.)

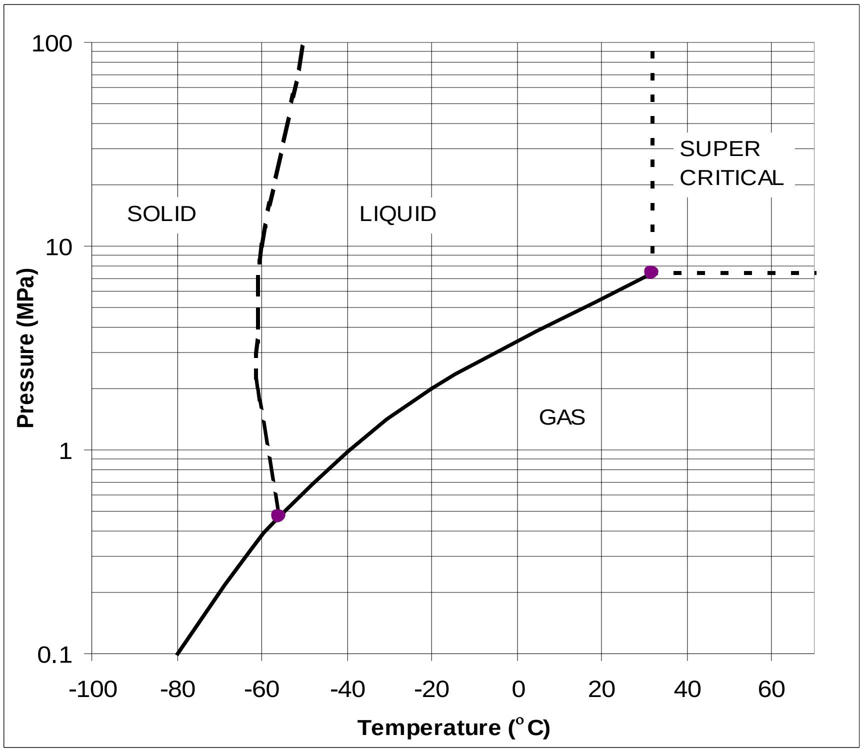


Figure 34. CO2 phase diagram, showing supercritical conditions at 32°C and 7.4 MPa. (after Bachu, 2000)

Hydrodynamic regime

Regional subsurface flow is generally expected to follow topography from recharge areas at the structural highs (i.e., domes and arches) to discharge areas at the structural lows (i.e., basins and embayments) created by large-scale tectonic events as conceptually illustrated for the study region in Figure 35. A more local example of this is shown in Figure 36, where the hydraulic gradient indicates that flow in the Wilcox formation moves toward and then follows the axis of the Mississippi Embayment rather than the Mississippi River itself. Flow in shallow aquifers will follow a more local trend, discharging to the river or to springs at the valley walls. In all cases, the TVA fossil plants are located in the valleys within local groundwater discharge zones. Deep aquifers may underflow the rivers, however, as groundwater moves toward a more distant discharge point as in the example in Figure 36. Thus it is important to assess the disposal site location relative to large-scale flow patterns rather than to local shallow flow systems. Injection at a site located near a structural high is preferable due to the extended flow path afforded, which offers the opportunity for hydrodynamic trapping to occur (Bachu, 2000). Hydrodynamic trapping occurs when the sweeping force due to groundwater movement exactly opposes the buoyancy force due to density differences between groundwater and the lighter CO_2.

In addition to large-scale tectonic features, local structural features such as fracture systems and faults can exert an effect on regional flow. This is apparent in the Valley and Ridge physiographic region, where groundwater moves along high-permeability fractures, solution cavities, and bedding planes (Figure 37). The general direction of flow is from the ridges to the valleys. Extensive vertical or high-angle fracturing and steeply-dipping bedding can both act to enhance vertical movement of formation fluids toward discharge in the valley where bypass might otherwise occur.

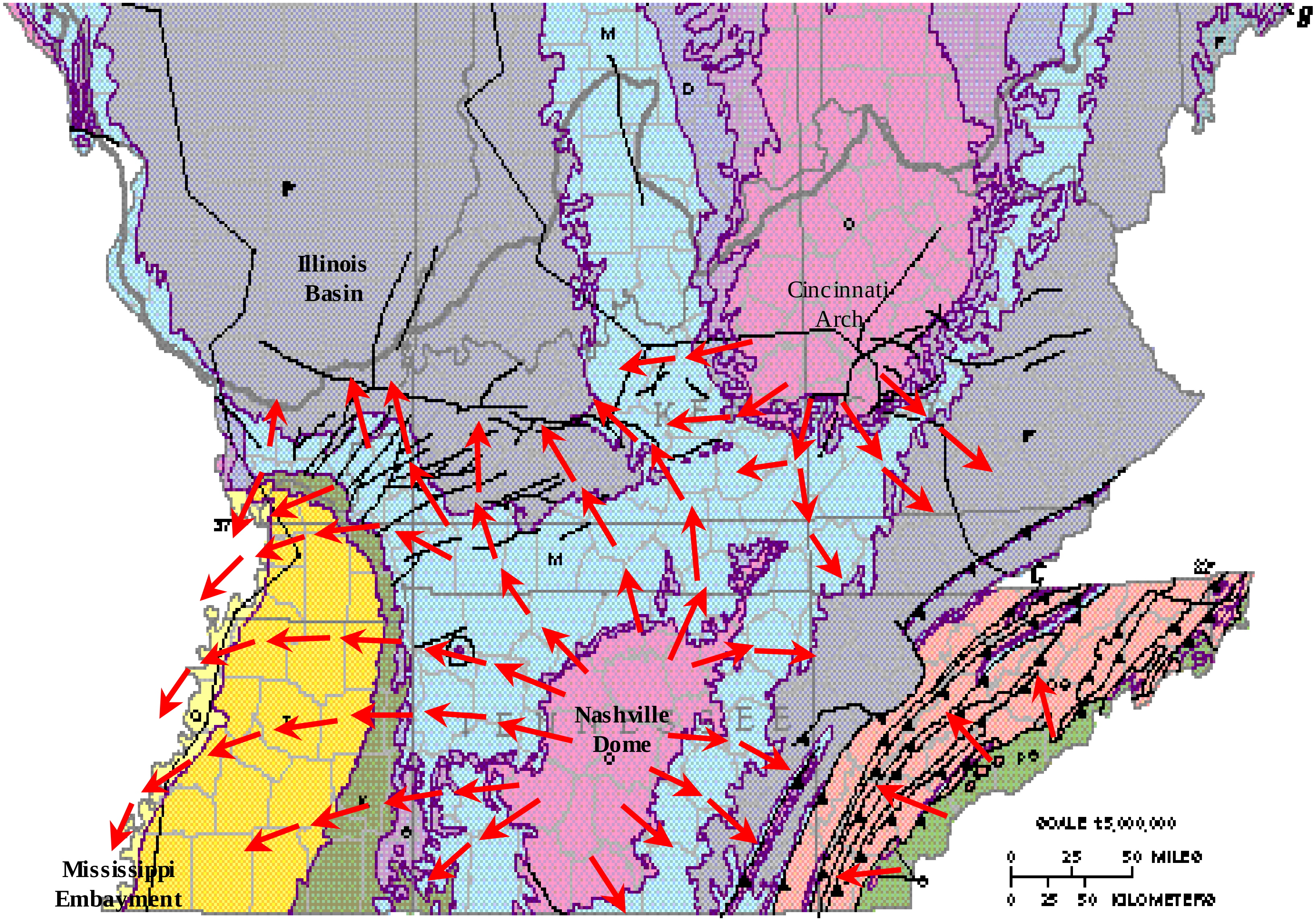
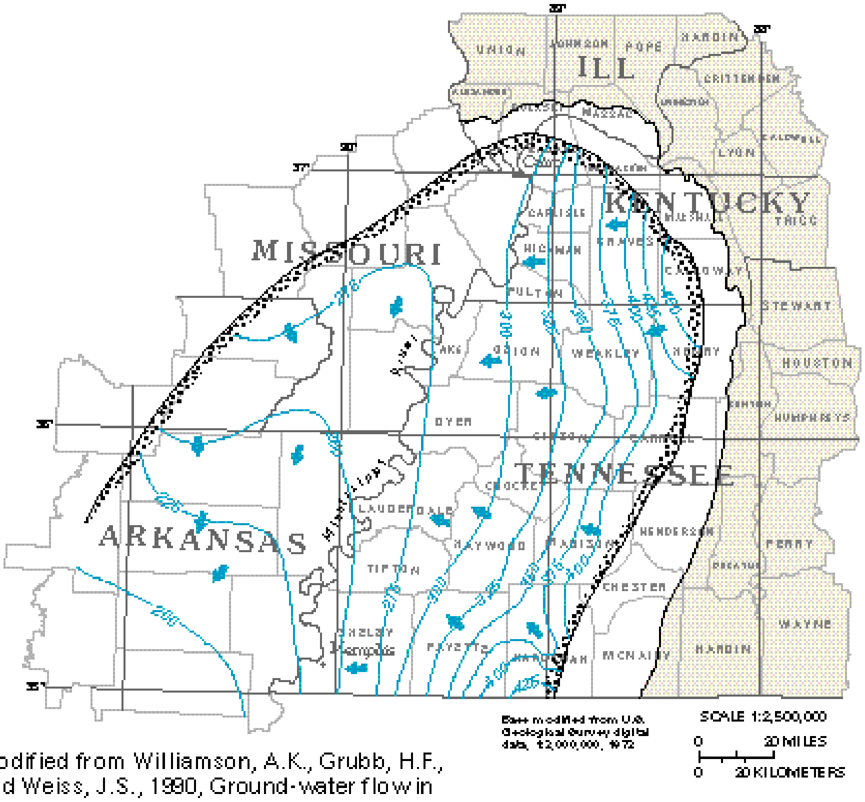


Figure 35. A generalized regional flow system based on an assumption of topographically-driven flow (Base map from Lloyd and Lyke, 1995).



Modified from Williamson, A.K., Grubb, H.F., and Weiss, J.S., 1990, Ground-water flow in the Gulf Coast aquifer systems, south-central United States—A preliminary analysis: U.S. Geological Survey Water-Resources Investigations Report 9–4071, 123 p.

EXPLANATION

▨ **Outcrop of lower Wilcox aquifer**

— 400 — **Potentiometric contour**—Shows altitude at which water level would have stood in tightly cased wells before development. Contour interval 25 feet. Datum is sea level

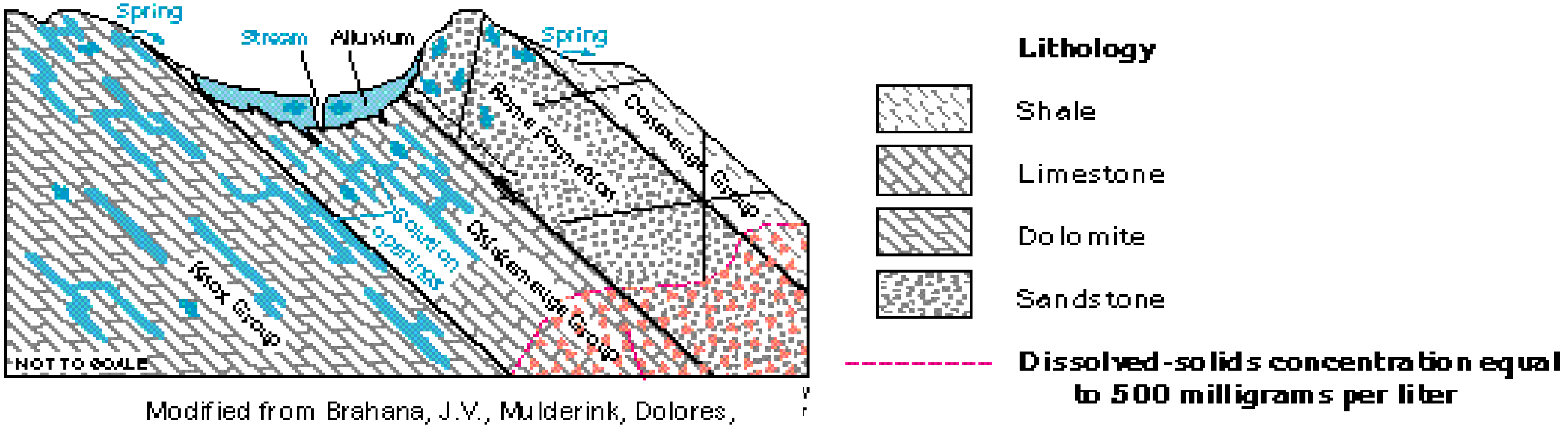
➡ **Direction of ground-water movement**

—— **Approximate limit of aquifer**

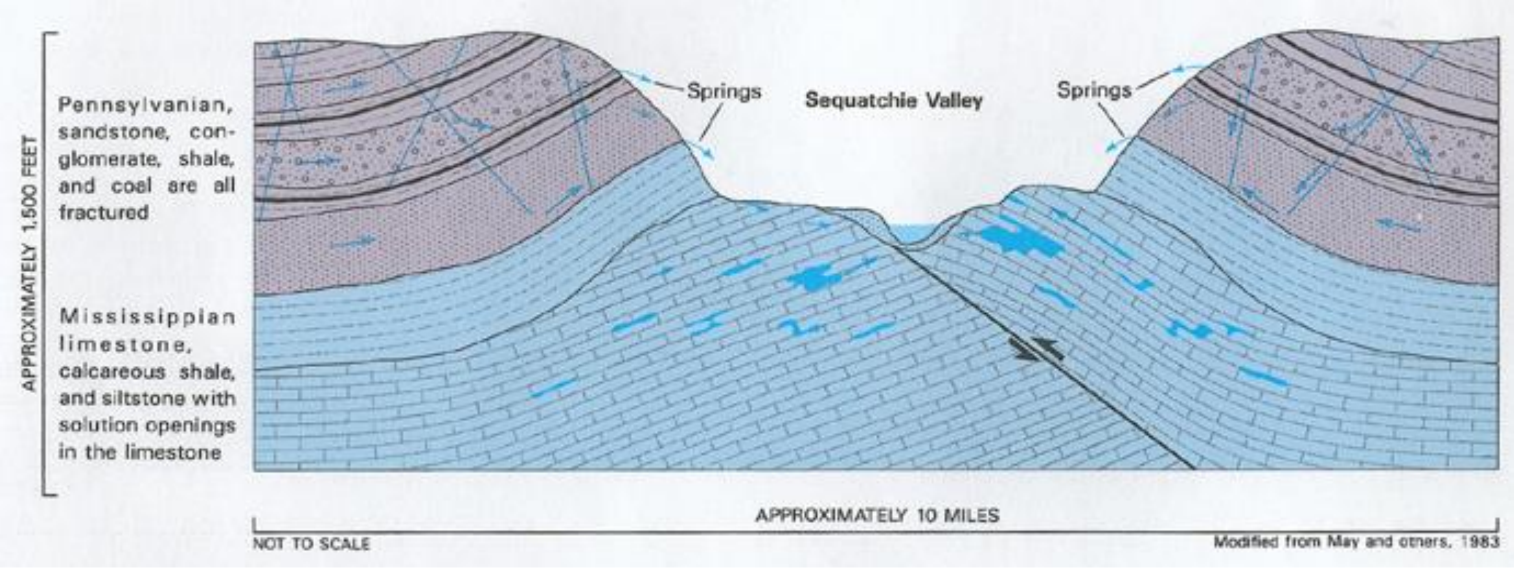
Figure 36. The regional direction of groundwater movement in the lower Wilcox aquifer is toward the axis of the Mississippi Embayment. The river acts as a discharge zone for shallower aquifers. However, groundwater from the Wilcox follows a more large-Scale trend toward the Gulf Coast. (From Lloyd and Lyke , 1995)

Permeable and porous zones for injection and sequestration

This is perhaps the most difficult criterion to assess in advance of a detailed site characterization due to the paucity of data from deep reservoir rocks at most locations. The definitive characterization occurs when a deep well is drilled on location, borehole logging is used to indicate porous zones and confining units, and permeability is measured by downhole pressure tests. Where deep test or production wells have been drilled nearby, the storage potential within target aquifers and the thickness of confining units can be determined by extrapolation. In the absence of this data, the best that can be done is an assessment of potential target zones based on general characteristics of the target formations where they have been measured in outcrop or shallower wells. In some cases, only the classification of geologic units as aquifers or confining units based on regional groundwater studies, such as those conducted by the U.S. Geological Survey and presented



Modified from Brahana, J.V., Mulderink, Dolores, Macy, Jo Ann, and Bradley, M.W., 1986, Preliminary delineation and description of the regional aquifers of Tennessee—The East Tennessee aquifer system: U.S. Geological Survey Water-Resources Investigations Report 82-4091, 30 p.



Modified from May and others, 1983

Figure 37. Groundwater flow in the Valley and Ridge system moves along fractures, solution cavities, and bedding planes from the ridges to the valleys. (Sequatchie Valley cross section corresponds to the location shown in Figure 23; from Lloyd and Lyke, 1995)

earlier (Figures 21-30), are available. For example, the Knox Group is classified as an aquifer everywhere across the study region, and oil and gas has been observed and in some cases produced from these rocks. This suggests that there are intervals within the Knox Group that are potential injection targets based on its general characteristics, but final evaluation would require testing at the sequestration site.

One can assign a minimum porosity and permeability, minimum aggregate thickness for aquifers, and minimum thickness for confining units necessary for a potential subsurface reservoir. Lloyd and Reid (1990) conducted a survey of liquid waste storage potential for Paleozoic rocks in the central and southern Appalachian Basin. The criteria they used in their study included: (1) minimum 5% porosity for reservoir rocks (sandstone, limestone, dolomite), (2) minimum aggregate thickness of 7.5 m within a 75-m interval for reservoir rocks, (3) minimum of 30 m of confining rock, and (4) a top of reservoir elevation of at least 300 m below sea level to prevent accidental penetration by water-well drilling. In his evaluation of conditions limiting CO_2 storage in aquifers, van der Meer (1993) added the criterion that permeability should be at least 0.050-0.100 μm^2. While the depth requirement is substantially greater for CO_2 disposal in order to reach supercritical conditions, as previously discussed, the other characteristics may be used as criteria for this application. These criteria do not address the characteristics required for storage of CO_2 in unmineable coal beds, which requires adsorption studies in order to determine efficiency and storage potential.

With the data obtained for this preliminary assessment, there is insufficient detail available in many cases to determine either the porosity or the aggregate thickness of porous zones, or both. Analysis of well logs where deep test wells have been drilled nearby could yield an estimate of both of these parameters for potential target zones, and is suggested as a first step in conducting a more detailed analysis of high priority sites.

Economic considerations

In most cases, a primary limiting economic condition would be transport of the CO_2 from the plant to the disposal site. For the purpose of this study, long-distance transport was not considered since local injection is assumed. There is potential economic gain for sites located near oil and gas fields or coal mines. A direct economic gain is the potential for enhanced oil, gas, or coal bed methane recovery as a result of CO_2 injection. The use of existing infrastructure (e.g., wells, pipelines) and data obtained during hydrocarbon production and mining activities can mitigate some of the cost of site setup and characterization, respectively. The number of wells required to make a sequestration target adequate and the depth to the target also factor into the assessment of whether or not a site is economically viable.

Socio-political considerations

The kinds of considerations that fall under this category include issues like environmental protection, public safety, and public assurance. These are not issues that could be addressed within the constraints of this preliminary report. However, state regulatory agencies need to be brought in early in the characterization and design phases in order to avoid later problems. Regulatory and public assurance is likely going to hinge on an injection design that includes some means of monitoring for leaks to overlying formations and to the atmosphere.

Site-specific information

In this section, local site-specific information is presented to the extent that it was available. The pros and cons for selection as a sequestration site are discussed for each plant.

Kingston Fossil Plant, Roane County, Tennessee

The Kingston fossil plant is located within the Valley and Ridge Physiographic Province, east of Pine Mountain Thrust Fault and immediately northwest of Watts Bar Lake on the Clinch River. The region is underlain by dipping thrusted and faulted rocks of the lower Paleozoic. The plant location can be found on the geologic map of the Harriman 7.5' Quadrangle, Tennessee (Moore et al., 1993). The area is underlain by the Cambrian Conasauga and Rome Formations which have been thrust over Mississippian and Silurian rocks along the Chattanooga fault.

A geologic cross section in the vicinity of the plant indicates approximately 2,000 feet of Conasauga thickness underlain by approximately 1,500 feet of Rome formation. In other locations in the state, the Rome Formation contains a basal sandstone lying immediately above crystalline basement that has been the target of assessment for deep liquid waste disposal. However, in this location the Rome Formation finds surface expression less than a mile from the plant due to the steep dip, and forms the ridge just northwest of Watts Bar Lake.

A thin package of Mississippian and Silurian sedimentary rock lies beneath the Chattanooga Fault which is, in turn, underlain by an unnamed regionally extensive thrust fault. Beneath that second fault are horizontal beds of Ordovician age beginning with the Sequatchie Formation. These flat lying strata are the most reasonable target for CO_2 injection because of their lateral extent and relative lack of deformation. If the sedimentary sequences have their maximum thickness in this region, then the top of the Knox Group would occur at roughly 5600 feet, well within the supercritical range for CO_2. The unnamed fault occurs within the Silurian Rockwood Formation, a primarily shale confining unit that can reach 780 ft thick within this region, providing a regionally extensive cap rock.

The Knox is a reasonable target in terms of storage potential based on general characteristics described for the Knox in nearby regions. It is one of the formations designated as an aquifer in every location where it is found (Figure 23). In addition, of the 6 test wells on record for Roane Co. at the Tennessee Division of Geology, three were noted to have gas shows in the Knox.

The pros then are flat laying rocks at depth, with potentially permeable rock sat a depth that is well beyond what is necessary for supercritical CO_2. Thick sequences of low-permeability interbedded carbonates and shales and an unknown thickness of Silurian shale can act as a confining layer. The primary con is that the region is intensely faulted, making knowledge of subsurface conditions and extrapolation from other locations difficult. Lloyd and Reid (1990) include this location in the region that they labeled as having no defined waste-storage potential due to thrust faulting and/or steeply dipping beds at the surface.

Bull Run Fossil Plant, Anderson County, Tennessee

The Bull Run fossil plant is located in the Valley and Ridge Province near Oak Ridge, Tennessee on the east shore of the Clinch River. The site can be found on the geologic map of the Clinton 7.5' Quadrangle, Tennessee (Swingle, 1964). Like the Kingston site, this location is underlain by a series of imbricate thrust faults. However this location is more intensely deformed, with beds dipping at roughly 45º at the surface and continuing beyond 4,000 ft below the surface. The plant is built essentially on top of a major tear fault that creates a 750-ft offset parallel to the Clinch River. Like the Kingston plant, this location is included in the region characterized as having no waste-storage potential due to the subsurface complexity.

The primary advantage of this site is the depth of knowledge about the subsurface characteristics. The site is located in close proximity to the Oak Ridge National Laboratory, where substantial geologic and hydrologic characterization has been conducted in support of environmental restoration activities. However, based on the structural complexity, the presence of significant vertical faulting, and steeply dipping strata with no confining layer, this is a very poor site to consider for CO_2 storage.

John Sevier Fossil Plant, Hawkins County, Tennessee

The John Sevier fossil plant is the third of the Tennessee plants to be located in the Valley and Ridge Province. The site is located 5 miles southeast of Rogersville along the Holston River, and can be found on the Geologic Map of Tennessee, Eastern Section (Hardeman et al., 1966). This region is underlain by Cambrian and Ordovician rocks beginning with the Chickamauga Group. There are 3 deep test wells on record at the Tennessee Division of Geology for Hawkins County. Very little information was available for these wells, however. Two of the three listed the top of the Sevier Shale at 1,670 ft, with the bottom of the formation at 5,920 ft and 7,250 ft (4,250-ft and 5,580-ft thicknesses, respectively). This formation is reported to range in thickness from 2,000 to 7,000 ft, which is consistent with the well log information. It is apparent that the target was the Chickamauga Group, which is an oil producer in the Swan Creek and Rose Hill fields to the northwest (Figure 33). However, facies changes have resulted in the formation trending from permeable limestones to low-permeability shales toward the southeast.

The Sevier Shale is part of the thick sequence of predominantly shale confining units in the middle and upper portion of the Chickamauga Group (Figure 23). This formation appears on the stratigraphic column as the confining unit immediately overlying the Knox Group. No information about dip angles is available, although the broad exposure of the Chickamauga at this location (approximately 10 miles perpendicular to strike) suggests a relatively low angle. This is underlain by the lower Ordovician Newala Formation, which is correlative with the gas-producing Mascot dolomite in the Swan Creek field. Data from the Swan Creek field cannot be directly extrapolated, however, because of facies changes and structural differences perpendicular to geologic strike.

It's likely that the upper Knox Group immediately underlying the Sevier Shale is porous and permeable, and that the Sevier Shale would provide a substantial confining unit to prevent cross-formational movement of the CO_2. However, it's not at all clear whether or not the CO_2 would simply migrate updip due to buoyancy forces and escape where the Knox outcrops to the northwest (see Hardeman et al., 1966) even though that opposes the direction of regional groundwater flow (Figure 36). If the top of the Knox were at roughly 7,000 ft as one of the deep tests suggests, then temperature and pressure conditions at the top of the reservoir would be 68ºC and 20 MPa, respectively. Under these conditions the density of supercritical CO_2 is around 0.7 g/cm^3 (Bachu, 2000), approaching the density of the formation waters and thus reducing the buoyancy force.

The characteristics that might make this a favorable sequestration site are the potential for significant porosity in the Knox Group with an overlying thick confining layer, and the presence of gas and oil in that same target zone in valleys to the northwest of the John Sevier site. The presence of economically producible gas and oil indicates that both sufficient porosity and a trapping mechanism exist at those locations. The potential sequestration target lies at a depth of around 7,000 ft which is favorable in terms of the CO_2 characteristics, but has the negative trade-off of increased drilling costs. The structural complexity that may be responsible for creating hydrocarbon traps also makes it difficult to extrapolate characteristics from one location to another, especially perpendicular to strike as in this case. This structural complexity argues against choosing this site as a high priority for further evaluation as a potential sequestration target.

Widows Creek Fossil Plant, Jackson Co., Alabama

The Widows Creek fossil plant is located in northeastern Alabama within the Sequatchie Valley portion of the Valley and Ridge Province (Figure 22). The information found about this region is sparse. Structurally, the region is an extension of the Appalachian foldbelt that extends northeastward through Tennessee and into southeastern Kentucky (Figure 20).

Figure 23 shows the stratigraphic sequences and hydrostratigraphic units for this region compared to those found in east Tennessee. The entire sequence from the upper Ordovician through the upper Cambrian is considered an aquifer, including the Knox Group which is an important aquifer and hydrocarbon-bearing unit to the north. A second deep aquifer is found at the base of the Cambrian, similar to the basal sandstones reported in Tennessee. The Upper Ordovician Sequatchie Limestone and Lower Cambrian Conasauga Formation can provide substantially thick confining units for these two aquifers, respectively.

However, there is little readily-available information about the deep subsurface in this region. Three wells were listed in a database provided on the Alabama Geological Survey's website (www.gsa.state.al.us). The wells were drilled to total depths of 1875-3935 ft, but no information was available regarding the purpose of the wells, formation depths, or the drilling targets. This does not mean that the information is nonexistent, only that it is not easily obtainable. It is possible that additional borehole information could be obtained by contacting the drilling contractors or site operators directly.

Given the scarcity of information about this site and the structural complexity in the Valley and Ridge Province in general, this site is not recommended as a priority site for further evaluation as there is simply too little known.

Gallatin Fossil Plant, Sumner Co., Tennessee

The Gallatin fossil plant is located on the northern flank of the Central Basin, which is underlain by the Nashville Dome (Figures 19 and 20). The plant is situated on the northern shore of the Old Hickory Reservoir of the Cumberland River, and can be found on the geologic map of the Laguardo 7.5' Quadrangle, Tennessee (Miller and Wilson, 1964). Bedrock in this region consists entirely of horizontal to gently-dipping Ordovician rocks (Figure 25). These rocks include the limestones of the Nashville and Stones River Groups, all of which have been characterized as too tight to be suitable as reservoirs for oil or gas (Mather, 1919). This is consistent with the USGS designation of the majority of these formations as confining units in Tennessee (Figure 25). The upper member of the Stones River Group and the Knox Group are both designated as aquifers. However, both are too shallow to be utilized for CO_2 injection.

However, the underlying Cambro-Ordovician rocks have been evaluated by DuPont for possible hazardous waste disposal. The DuPont Old Hickory Plant #1 (41-037-8) was drilled in 1969 to a total depth of 5446 ft, which penetrated pre-Cambrian basement. The top of the Knox group was observed at 1068 ft, and a basal sandstone (possibly the Rome Formation or its equivalent) was observed at 5270 ft. This basal unit was the proposed injection zone, and 35 cores were obtained between depths of 5270 ft and 5462 ft. Most were characterized as fine grained sand with an average porosity of 9.2% (1.7-14.9%) and an average permeability of 15.9 md (0.1-132 md). The site was deemed "not feasible for injection", according to records of public hearings, due to the need for hydrofracturing to maintain the desired injection rates. The proposed injection rates were not found in those records, however. The DuPont well is located approximately 20 miles west of the Gallatin plant and the depth to equivalent horizon is likely to be slightly less at the Gallatin site based on low dip angles.

Due to the relatively shallow depth to crystalline basement, the only potential injection zones are in the Cambrian rocks. The characteristics from the core samples would seem to indicate adequate porosity and permeability for deep injection, although the thickness of permeable zones and therefore the storage capacity is unknown. The depth of the basal sand is sufficient for supercritical conditions. Groundwater is expected to flow away from the central basin toward bedrock lows in Kentucky. All of those characteristics would make this site favorable for CO_2 injection.

Johnsonville Fossil Plant, Humphreys Co., Tennessee

The Johnsonville fossil plant is located at the boundary between the Western Valley and Western Highland Rim physiographic units (Figures 19 and 20). Here the stratigraphy changes dramatically on either side of the Tennessee River. The plant is located just east of the Tennessee River, and can be found on the geologic map of Tennessee, West-Central sheet (Miller et al., 1966). Bedrock immediately beneath the site is the Mississippian Chattanooga Shale and Fort Payne Formation.

Locally, shallow groundwater no doubt discharges to the Tennessee River. For topographically-driven flow, deep groundwater would be expected to underflow the river and move from the Nashville Dome westward toward the Mississippi Embayment. Thus, the location within or near the recharge areas of the Central Basin is favorable for CO_2 injection.

Five deep wells were drilled by DuPont in close proximity to the Johnsonville site for use in hazardous waste disposal. Total depth of these wells was between 6500 and 7500 ft., with crystalline basement identified at 7455 ft. Several evaluations were conducted in these wells including geophysical logging, tracer tests, drill stem tests, and coring. Most of the data from these tests were not available at the Tennessee Division of Geology offices, but it may be possible to obtain copies of data and logs directly from DuPont.

The top of the Knox Group is located at 1650 ft, based on borehole logs. Other formation tops that were identified include the Conasauga (5640 ft), the “basal massive carbonate” (7148 ft), and the basal sand (7210 ft). These rocks are not included in the stratigraphic column on the geologic map for this area because none of them outcrop in the area, and facies changes make it difficult to correlate to these formations in the eastern part of the state.

It appears that the shallowest zones tested were in the lower Knox at depths of 4400-5400 ft, in the Conasauga at depths of 6000-6400 ft, and in the basal carbonate and sand from 7150-7180 ft. Although the tracer test and drill stem test data are not available, the fact that they tested these zones indicated that there was good reason to believe that they were permeable zones. Core analyses show a very good zone in the lower Knox at 4410-4448 ft. In this core, permeability was 110 md and porosity was 10.7%. A second good zone was present in the Conasauga at 6038 ft, with a permeability of 27 md and porosity of 5.2%. Other core samples had reasonable permeability values (~5-10 md) but only 1-2% porosity.

Given all of the factors described above, this site looks like a very good possibility for CO_2 storage. It would be useful to obtain as much data from DuPont as possible, particularly if they have used these wells for disposal of liquid wastes and can provide information about injection rates and volumes stored.

Cumberland Fossil Plant, Stewart Co., Tennessee

The Cumberland fossil plant is located within the Western Highland Rim physiographic unit (Figure 19), on the northwestern flank of the Nashville Dome. The site lies on the south bank of the Cumberland River and can be found on the Geologic Map of the Cumberland City 7.5’ Quadrangle, Tennessee (Tiedemann et al., 1968). Mississippian aquifers of the Interior Low Plateaus Province generally subcrop in this region (Figure 26). From a regional flow and tectonic stability point of view, this site is ideal for consideration as a sequestration site. However, the plant is located at the center of a very large impact crater, and the subsurface immediately beneath the plant is deformed and highly brecciated.

Upwarping at the center of the crater has resulted in erosion of the younger strata, and Ordovician rocks are exposed at the surface. Concentric circular faults ring the site out to a radius of nearly 5 miles.

It is possible that the faults could serve as compartment seals, restricting lateral movement. CO_2 could be transported less than a mile in order to get outside of the central brecciated portion of the structure. However, the Knox Group is only 2,500 ft deep in this area which is just at the minimum depth for supercritical CO_2. Although the lower half of the overlying Stones River Group is classified as a confining unit in central Tennessee (Figure 25), any upward migration could result in a phase change with rapid loss of gaseous CO_2. In addition, the permeability of the faults and their potential to act as conduits for vertical flow and release of CO_2 is unknown. These characteristics make this site unsuitable for sequestration.

Allen Fossil Plant, Shelby Co., Tennessee

The Allen fossil plant is located in the Coastal Plain Physiographic Province which is associated with the Mississippi Embayment (Figure 20). The plant is on the south bank of Lake McKeller which empties into the Mississippi River one mile downstream. The city of Memphis is immediately across the lake to the northeast, and the site can be found on the geologic map of the Fletcher Lake 7.5' Quadrangle, Tennessee (Hart, 1979).

The region is underlain by Quaternary, Tertiary, and Cretaceous sediments that thicken toward the axis of the Mississippi Embayment (Figure 28). Regional groundwater movement is west toward the river, but groundwater from the Lower Wilcox aquifer does not discharge to the river (Figure 35). Instead, potentiometric contours indicate that groundwater at this depth underflows the river and follows the axis of the structural basin toward the Gulf Coast. This suggests that flow in the deeper rocks underlying these semi-consolidated sediments will follow the same general pattern.

Unfortunately, the geologic cross section and representative geologic column only extend down through the Tertiary Memphis sand, a depth of less than 1,000 ft. However, two wells were drilled in Shelby Co. north of the Allen plant but roughly the same distance from the river and, therefore, potentially correlative. The Appalachian Oil & Gas Mitchell #1 (41-157-20003RI) was drilled to a total depth of 9,250 ft. A stratigraphic marker in the Cretaceous was noted at 3230 ft, and the top of the Conasauga Formation was listed at 7550 ft. If the top of the Wilcox Formation is a reflection of the shape of the downwarping bedrock (Figure 30), then the stratigraphy at the Allen site is likely to be very similar to that at the drill site. A second well, the Roy Lovelace Miller #1 (41-157-20002), was drilled to a total depth of 3,993 ft further south. No well records were located for this well at the Division of Geology offices, but the Summary of Deep Tests in Tennessee lists this well as penetrating the Paleozoic and as having been completed as a shut in gas well. Gas was reported at depths between 3232-3342 ft, in Cretaceous sediments, the identical depth at which the stratigraphic marker was noted in the other well. This suggests that there is a unit at roughly 3200 ft depth that is permeable and porous enough to sustain gas production and is, therefore, a potential candidate for CO_2 injection as well. The depth is sufficient for supercritical conditions for CO_2.

The geologic map indicates an erosional unconformity cutting through the Cretaceous sediments. Mississippian and older formations appear immediately below the unconformity. This is consistent with the core descriptions for the Miller #1 well, where an unconformity occurs at 3338 ft, immediately below the gas-producing zone. However, the stratigraphic section in the vicinity of the Mississippi River is not delineated. The Cretaceous rocks outcrop at the easternmost edge of the Coastal Plain region, indicating strata that gently dip from the central part of the state toward the Mississippi Embayment. That means that lateral movement updip over a considerable distance under buoyancy force would be required in order to impact groundwater sources. It also means that lateral spread of a plume of CO_2 injected into the permeable Cretaceous interval is not likely to reach depths at which a phase change will occur, should movement go counter to regional groundwater flow.

The lack of detailed information on the stratigraphic section below the Tertiary aquifers hinders a full evaluation of the storage potential at this site. However, based on the above discussion, this site appears to be a reasonable candidate for further evaluation.

Shawnee Fossil Plant, McCracken Co., Kentucky

The Shawnee fossil plant is situated in a very similar geologic environment as the Allen plant discussed above. The plant is located in western Kentucky on the Ohio River just west of Paducah, Kentucky. The site occurs at the northern reach of the Mississippi Embayment (Figure 30). Here, the Lower Wilcox aquifer is found at shallower depths, and regional flow follows the axis of the Embayment. Stratigraphic information can be found on the geologic map of the Joppa 7.5' Quadrangle, McCracken County, Kentucky (Finch, 1967). The map is available in electronic format at the Kentucky Geological Survey website (www.uky.edu/KGS).

Very detailed information can be found for the shallow subsurface down to a few hundred feet. But available information about the deeper bedrock was scarce. There are 5 wells located in the portion of the Joppa Quadrangle located in McCracken Co. The stratigraphic section included on the geologic map extends only through the uppermost Cretaceous, which is found only a few hundred feet below the surface in the vicinity of the plant. Therefore the permeable zone in the Cretaceous sequence that is a potential injection target at the Allen site is not suitable at this site. In the well records, formation tops are reported down to the base of the Devonian Jeffersonville Limestone at a depth of 1273 ft., the apparent oil or gas target. Although the Jeffersonville Limestone and the overlying Sellenburg Limestone (confined by 300 ft of New Albany Shale) could provide a potential sequestration target if porosity and permeability were sufficient, the depth is too shallow for CO_2 injection. No information about deeper strata was found that would allow an assessment of the storage potential at this site. Given the lack of information at the depths of interest, this site would not be considered a high priority for further investigation.

Colbert Fossil Plant, Colbert Co., Alabama

The Colbert fossil plant is located in northwestern Alabama on the southern flank of the Nashville Dome. The location is considered part of the Interior Low Plateaus Province which extends into Tennessee and northern Kentucky and presents as a wide band surrounding the Nashville Dome (Figure 24). Topographically-driven flow would be expected to move from recharge areas on the Dome through the Interior Low Plateaus and toward structural basins that underlie the Coastal Plain to the south and west (Figure 21b).

The area is underlain by Mississippian-age sediments and the Lower Mississippian Chattanooga Shale, which is an important confining unit for deep groundwater as well as hydrocarbons in some locations, extends into this region. However, very little is known about the deep subsurface. There are no deep wells listed for this area in the Alabama Geological Survey's database, and no information was found on the deep subsurface geology at the depths of interest. Older Geological Survey publications written about the geology of Colbert County are no longer available through the Survey.

With additional time it might be possible to locate out-of-print publications that address the geology of this region, and the University of Alabama geology department and libraries would be a good starting point. The location of this plant in a tectonically stable region suggests that it could be worth consideration as a possible CO_2 injection site. However, the amount of additional time required to obtain the information needed to properly evaluate the site and the lack of deep borings in the vicinity make it a very low priority for further consideration at this time.

Paradise Fossil Plant, Muhlenberg Co., Kentucky

The Paradise steam plant is located in southwestern Kentucky on the western shore of the Green River. The site is situated on the western flank of the structural highs that make up the Nashville Dome and the Cincinnati Arch (Figure 18). These two structures effectively create a deep groundwater divide, with regional flow on the western side moving generally from this structural high toward the Illinois basin to the northeast.

The site can be found on the geologic map of the Paradise 7.5' Quadrangle, Kentucky, which is available in electronic format through the Kentucky Geological Survey's website (www.uky.edu/KGS). The shallow subsurface is underlain by Pennsylvanian sandstones and shales, which make up the majority of freshwater aquifers and confining units in this region (Figure 27). Erosional patterns indicate that the sediments are relatively flat-lying.

The Paradise plant site is located within the western Kentucky coalfields, and in an important gas and oil producing region. Numerous gas and oil wells are located within the region (Figure 31). Many of the wells are included in the Tertiary Oil Recovery Information System (TORIS), a public database maintained by the National Petroleum Council and used by the U.S. Department of Energy for assessing domestic oil reserves. The significance of this is that a large amount of drilling and test data is available to the public. The Kentucky Geological Survey also maintains a database of information from drilling operations and a core repository. Many of the records have been scanned and are available through an interactive search engine on the Survey website. A search of wells within the Paradise Quadrangle brought up 27 records for wells completed between 1930 and 1984. Most of the wells were drilled to targets in the Mississippian strata at depths of 2500 ft or less; two were drilled to depths exceeding 3500 ft in Silurian strata, providing lithologic information below the depth to supercritical CO_2. Many more wells are located within the adjacent quadrangle regions to the west of the Paradise plant. Therefore, the availability of the kind of data necessary to evaluate the site in detail is good. The region is also underlain by the economically important Carbondale Formation, which has been extensively mined for coal (Figure 32; Andrews et al., 2000). Thus information from mining operations, which would include detailed structural mapping, is also available.

It is suggested that this site be given the highest priority for further evaluation as a CO_2 injection site due to many favorable conditions. The site is located in a tectonically stable region where deep groundwater flow is likely to have long flowpaths. Extensive mining as well as gas and oil production has resulted in a substantial data base for identifying and characterizing potential subsurface injection targets. The proximity of the site to drilling operations opens up the possibility for using existing infrastructure for injection. The presence of hydrocarbons means that structural traps exist so that there is less reliance on hydrodynamic trapping. There is a possibility of using deep saline reservoirs, deep coal seams, or depleted hydrocarbon reservoirs as injection targets, perhaps even using multiple targets to research sequestration effectiveness and subsurface dynamics.

Summary and ranking

The following table lists the TVA fossil plant locations in order of greater to lesser suitability as potential CO_2 sequestration sites:

Table 5. TVA fossil plant sites ranked according to suitability for CO_2 sequestration.

Plant	Rating	Comments
Paradise	Very Good	Best candidate due to favorable geologic characteristics and wealth of available data. Potential use of existing well infrastructure. Potential for multiple targets (brine formation, oil or gas reservoir, or coal bed storage).
Johnsonville	Very Good	Favorable geology for underground storage and availability of deep well data. Favorable location within deep groundwater flow system.
Gallatin	Favorable	Favorable geologic characteristics, although detailed subsurface geology is less well known.
Allen	Marginal	Insufficient data to fully evaluate potential targets at depth. Reasonable candidate for additional evaluation if primary choices are found unsuitable. Long transport pathways to potential discharge locations.
Kingston	Marginal	Favorable formations at depths below the Chattanooga Fault, but deep disposal is required. Shallower horizons are complexly faulted.

Widows Creek	Marginal	Limited data, but underground structural complexity is likely based on location in the Appalachian fold belt.
Colbert	Potential	Potentially favorable geologic characteristics based on tectonic setting. However, subsurface data not available to evaluate the potential as good or poor.
Shawnee	Poor	Unfavorable geology for underground storage. Low priority for additional evaluation.
John Sevier	Poor	Underground structural complexity.
Bull Run	Poor	Significant vertical faults at and near the plant and steeply-dipping stratigraphy.
Cumberland	Poor	Marginal depth for injection at supercritical conditions. Complex structure associated with impact crater. Permeability of faults could be conduit for CO_2.

The sites that are given the highest priority for further evaluation as CO_2 injection test sites are the Paradise Fossil Plant in Muhlenberg County, Kentucky, and the Johnsonville fossil Plant in Humphreys County, Tennessee. The Paradise site has potential for sequestration in any or all of coalbeds, saline reservoirs, and depleted oil or gas reservoirs. The Johnsonville site would be restricted to saline reservoir sequestration. Both have deep well information available. In both areas issues of permitting and regulatory acceptance are likely to be eased by previous or ongoing activities – hydrocarbon production in the case of the Paradise site, and deep hazardous waste disposal in the case of the Johnsonville site. Both show evidence of porous and permeable zones at a depth that is sufficient for supercritical CO_2.

Additional work is required to obtain the detailed data necessary to further evaluate these sites. It may be necessary to establish contact with site owners where drilling operations have been conducted in order to obtain welltest data and borehole logs. However, this preliminary investigation indicates that both of these sites have good potential.

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Holloway, S., and D. Savage, 1993. The potential for aquifer disposal of carbon dioxide in the UK. Energy Conv. Mgmt., v. 34, p. 925-932.

Hosman, R.L., Weiss, J.S., 1991, Geohydrologic units of the Mississippi embayment and Texas Coastal Uplands aquifer systems, south-central United States: U.S. Geological Survey Professional Paper 1416 – B, 19 p.

Lambert, T.W., 1967. Paducah West and Paducah East Quadrangle (McCracken Co. and Illinois). USGS Hydrologic Investigations Atlas (USGS HA-177), Pub. No. 1628.

Lloyd, O.B., Jr., 1990. Evaluation of liquid waste-storage potential based on porosity distribution in the Paleozoic rocks in central and southern parts of the Appalachian Basin. USGS Report P 1468.

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Miller, R.A., and C.W. Wilson, Jr., 1964. Geologic Map of the Laguardo Quadrangle, Tennessee. State of Tennessee, Division of Geology GM313-SW.

Moore, J.L., C.P. Finlayson, and R.C. Milei, 1993, Geologic Map and Mineral Resources Summary of the Harriman Quadrangle, Tennessee. State of Tennessee Division of Geology, MRS 123-NE and GM 123-NE.

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Stearns, R.G., and C.A. Armstrong, 1955. Post-Paleozoic Stratigraphy of Western Tennessee and Adjacent Portions of the Upper Mississippi Embayment. Prepared in cooperation with U.S. Geological Survey.

Swingle, G.D., 1964. Geologic Map of the Clinton Quadrangle, Tennessee. State of Tennessee Division of Geology, GM 137-SW.

Tiedemann, H.A., C.W. Wilson, Jr., and R.G. Stearns, 1968, Geologic Map and Mineral Resources Summary of the Cumberland City Quadrangle, Tennessee. State of Tennessee Division of Geology, GM 38-NW and MRS 38-NW.

van der Meer, L.G.H., 1993. The conditions limiting CO_2 storage in aquifers. Energy Conv. Mgmt., v.34(9-11), p.959-966.

Appendix: Resource Listing

General Resources:

Kentucky

- Kentucky Geological Survey website (www.uky.edu/KGS) – contains downloadable electronic versions of geologic maps, water resource maps, oil and gas well records (including borehole logs), KGS bulletins
- Lloyd, O.B., and W.L. Lyke, 1995. Groundwater Atlas of the U.S.: Illinois, Indiana, Kentucky, Ohio, and Tennessee. HA 730-K, U.S. Geological Survey (available online in electronic format).
- Hopkins, H.T., 1966. Fresh-saline water interface map of Kentucky. Kentucky Geological Survey (MISCM 21), Pub. No. 1108.

Tennessee

- Tennessee Dept. of Environment and Conservation, Division of Geology website – contains publications catalog but no electronic documents
- Hardeman, W.D., R.A. Miller, and G.D. Swingle, 1966. Geologic Map of Tennessee, East Sheet. State of Tennessee Division of Geology.
- Miller, R.A., W.D. Hardeman, D.S. Fullerton, C.R. Sykes, and R.K. Garman, 1966. Geologic Map of Tennessee, West-Central Sheet. State of Tennessee Division of Geology.
- Swingle, G.D., R.A. Miller, E.T. Luther, W.D. Hardeman, D.S. Fullerton, C.R. Sykes, R.K. Garman, 1966. Geologic Map of Tennessee, East-Central Sheet. State of Tennessee Division of Geology.
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- Lloyd, O.B., and W.L. Lyke, 1995. Groundwater Atlas of the U.S.: Illinois, Indiana, Kentucky, Ohio, and Tennessee. HA 730-K, U.S. Geological Survey (available online in electronic format).
- Newcome, R., Jr., 1958. Ground Water in the Central Basin of Tennessee. State of Tennessee Division of Geology, Report of Investigations No. 4, 81 pp.
- Piper, A.M., 1993. Ground Water in North-Central Tennessee. U.S.G.S. Water-supply Paper 640.

Alabama

- Geological Survey of Alabama website (www.gsa.state.al.us) – contains electronic versions of geologic maps and recharge areas for major aquifers that can be viewed using an interactive reader; searchable publications catalog but no electronic documents
- Miller, J.A., 1990. Groundwater Atlas of the U.S.: Alabama, Florida, Georgia, and South Carolina. HA 730-G, U.S. Geological Survey (available online in electronic format).

Resources by Site:

1. John Sevier Steam Plant (Hawkins Co., TN)

Deep well locations (TN Division of Geology):

- Amoco Production Co. #1 (41-073-20001); 5703’ to Cambrian
- Eastern American Energy #18 (41-073-20005); 7250’ to Ordovician
- Eastern American #1-5 (41-073-20004); 5920’ to Ordovician

Other resources:

- Lloyd, O.B., Jr., 1990. Evaluation of liquid waste-storage potential based on porosity distribution in the Paleozoic rocks in central and southern parts of the Appalachian Basin. USGS Report P 1468.
- Hatcher, R.D., Jr., R.T. Williams, and M.W. McCown, 2001. Swan Creek field: Isolated success or tip of the iceberg? Oil & Gas Journal, Oct. 1, 2001, p.38-44.
- TVA, 1969. John Sevier Steam Plant Final Design Report, TVA Technical Report No. 32-200.
- Rodgers, J., and D.F. Kent, 1948. Stratigraphic Section at Lee Valley, Hawkins County, Tennessee. Tennessee Division of Geology, Bulletin 55, 45 pp.

2. Bull Run Steam Plant (Anderson Co., TN)

Deep well locations (TN Division of Geology):

- Mohawk Oil Lines #1 (41-001-6); 3480’ to Cambrian
- Arco Oil and Gas #1 (41-001-20007); 11,540’ to Precambrian

Other resources:

- Hatcher, R.D., Jr., P.J. Lemiszki, R.B. Dreier, R.H. Ketelle, R.R. Lee, D.A. Leitzke, W.M. McMaster, J.L. Foreman, and S.Y. Lee, 1992. Status Report on the Geology of the Oak Ridge Reservation. ORNL/TM-12074. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 244 pp.
- Solomon, D.K., G.K. Moore, L.E. Toran, R.B. Dreier, and W.M. McMaster, 1992. Status Report: A Hydrologic Framework for the Oak Ridge Reservation. ONRL/TM-12026, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
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- TVA, 1967. The Bull Run Steam Plant: A Report on the Planning, Design, Construction, Costs, and First Power Operations of the Initial One-Unit Plant, TVA Technical Report No. 38.

3. Kingston Steam Plant (Roane Co., TN)

Deep well locations (TN Division of Geology):

- Shell Oil Co. #1 (41-035-12); 5405’ to Knox.
- Ladd Petroleum Co. #1 (41-035-20041); 10,141’ to Precambrian

- ARCO #1 F.J. Jewett (41-035-20132); 8500’ to Rome Fm.
- ARCO #1 Simonton et. al. (41-035-20163); 7400’ to Conasauga
- ARCO #1 Wright (41-143-20022); 7200’ to Conasauga; D&A
- Kneten Oil Co. #1 (41-143-20023); 4500’ to Knox

Other resources:

- TVA, 1965. The Kingston Steam Plant: a Report on the Planning, Design, Construction, Costs, and First Power Operations, TVA Technical Report No. 34.

4. Gallatin Steam Plant (Sumner Co., TN)

Deep well locations (TN Division of Geology):

- Dupont (Old Hickory Plant) #1 (41-037-8); 5574’ to Precambrian

Other resources:

- TVA, 1967. The Gallatin Steam Plant: A Report on the Planning, Design, Construction, Costs, and First Power Operations of the Initial Four-Unit Plant, TVA Technical Report No. 36.

5. Cumberland Steam Plant (Stewart Co., TN)

Deep well locations (TN Division of Geology):

Other resources:

- TVA, 19??. Cumberland Steam Plant Final Design Report, TVA Technical Report No. 40.

6. Johnsonville Steam Plant (Humphreys Co., TN)

Deep well locations (TN Division of Geology):

- Dupont & Co. #1 (41-085-1); 6735’ to Cambrian dol.; disposal well
- Dupont & Co. #2 (41-085-2); 7461’ to Precambrian arkose; disposal well
- Dupont & Co. #3 (41-085-3); 6340’ to Camb. dol.; disposal well
- Dupont & Co. #4 (41-085-4); 6502’ to Camb. dol.; disposal well
- Dupont & Co. #5 (41-085-20001); 7000’ to Camb. dol.; disposal well
- Dupont & Co. #6 (41-085-20003); 6508’ to Camb. dol.; disposal well

Other resources:

- Webster, D.A., J.R. Macconi, D.E. Stehle, and D.J. Collins, 1993. Subsurface geology and hydraulic data from 769- to 8,765-feet depth at the Johnsonville-site study well, Humphreys County, Tennessee. USGS, Nashville, TN.

- TVA, 1958. The Johnsonville Steam Plant: A Report on the Planning, Design, Construction, Costs, and First Power Operations of the Initial Six-Unit Plant. TVA Technical Report No. 31.

7. Allen Steam Plant (Shelby Co., TN)

Deep well locations (TN Division of Geology):

- Appalachian Oil and Gas #1 (41-157-20003R1); 9250' to Conasauga
- Roy Lovelace #1 (41-157-20002); 3993' to Paleozoic

Other resources:

- Stearns, R.G., and C.A. Armstrong, 1955. Post-Paleozoic Stratigraphy of Western Tennessee and Adjacent Portions of the Upper Mississippi Embayment. Prepared in cooperation with U.S. Geological Survey. (Environmental relationships, electric-log correlations, isopach, sand distribution, and structural data on 5 key post-Paleozoic units.)

8. Paradise Fossil Plant (Muhlenberg County, KY)

Deep well locations (Kentucky Geological Survey):

(Numerous wells - see Fig. 16; KGS website has listing by geologic quadrangle map)

Other resources:

- Carey, D.I., and J.F. Stickney, 1989. Ground-water Resources of Muhlenberg County, Kentucky. KGS Open-File Report OF-01-89.
- Hopkins, H.T., 1966. Fresh-saline water interface map of Kentucky. KY Geol. Surv. (MISCM 21), Pub. No. 1108.
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- Carey, D.I., and J.F. Stickney, 1979. Ground-water Resources of McCracken County, Kentucky. Kentucky Geological Survey Open-File Report OF-01-79.

9. Shawnee Steam Plant (McCracken Co., KY)

Deep well locations (Kentucky Geological Survey):

- Gibbs et al. #1 (Permit No. 72363); to Paleozoic
- Gibbs #1 (Permit No. 69884); 1273' to Devonian Jeffersonville LS
- Gibbs #2 (Permit No. 72216); 3260' to Ordovician
- Rudolph #1 (Permit No. 71730); 2856' to Ordovician Knox Grp.
- Rudolph #2 (Permit No. 73847); total depth unknown

Other resources:

- Lambert, T.W., 1967. Paducah West and Paducah East Quadrangle (McCracken Co. and Illinois). USGS Hydrologic Investigations Atlas (USGS HA-177), Pub. No. 1628.
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10. Colbert Steam Plant (Colbert Co., AL)

Deep well locations: (Geological Survey of Alabama): None found.

Other resources:

- TVA, 1963. The Colbert Steam Plant: A Report on the Planning, Design, Construction, Costs, and First Power Operations of the Initial Four-Unit Plant, TVA Technical Report No. 29-200.

11. Widows Creek Steam Plant (Jackson Co., AL)

Deep well locations: (Geological Survey of Alabama):

- Talley #1 (2059); drilled to 3935’;
- Allison #1 (2063); drilled to 2483’;
- Thelma-Marshall 36-7 #1 (3669); drilled to 1875’

Other resources:

- TVA, 1965. The Widows Creek Steam Plant Units 1-6: A Report on the Planning, Design, Construction, Costs, and First Power Operations of the Initial Six-Unit Plant, TVA Technical Report No. 32.

- TVA, 1971. The Widows Creek Steam Plant Units 7 and 8: A Report on the Planning, Design, Construction, Costs, and First Power Operations of the Two-Unit Addition, TVA Technical Report No. 33.