

HYDROGEN RICH GAS STORAGE
IN SEDIMENTARY FORMATIONS

by

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1. Large scale energy storage. Energy storage is becoming a problem of increasing importance not only with regard to renewable energy sources but also to nuclear power. This is because as more electrical power is produced by nuclear means the role of the nuclear station moves from being a base load plant towards providing also the power peaks of short duration. Since nuclear stations are expensive (although low in running costs) it is clearly economically unfavourable to employ some of them only during periods of peak demand and to have them idle the rest of the time. Such a situation would be avoided if a smaller number of nuclear plants could be employed in conjunction with an economical means of storing some of the energy, output of the nuclear stations in times of surplus for use during times of peak demand.

With regard to renewable sources such as wind and solar it is not so much the variability of the consumer that is the problem but rather the source. The reason for requiring storage is as before: to reduce the capital equipment otherwise required to be on standby to meet consumers' demands. This capital equipment is likely to be the plant of a back-up non-renewable energy source.

Energy storage is required over two time scales which may be described as diurnal and seasonal. Diurnal refers to the day-night cycle of demand and also of supply in the case of solar energy. If solar energy could be relied upon every day, demand and supply would match fairly well more so than in the case of nuclear energy. Seasonal refers to longer term variations in demand due to the heating load in winter, for example, and the air conditioning load in summer, as well as shorter periods down to a week or so characterised by the

cold spell or heat wave. Seasonal also refers to variations of similar time span in renewable sources: the summer-winter variations as well as the occasional period of several consecutive cloudy or windy days.

It is apparent that effective storage for renewable sources must be thought of in terms of the seasonal time scale. However the cost of storage, which is an additional capital item, must always be compared with the costs of the additional energy plant which one is trying to save through the use of storage. In the case of the solar ammonia scheme the major capital cost of long term storage is the value one puts on the stored synthesis gas. This capital item must be compared with the alternative of providing additional collectors for gathering energy during winter (which may be idle during summer unless they are used for manufacturing a storable by-product such as ammonia). An optimum amount of storage for the solar ammonia scheme is about 20 days (on the basis of providing the base load continuously from storage alone).

2. Solution. Mankind has always solved its large scale storage problems by turning to nature. Water is stored by damming naturally occurring valleys; natural gas, while occurring in natural underground reservoirs, is routinely restored in other underground reservoirs such as disused gas wells or aquifers. In Australia at Gidgealpa gas is processed and restored underground to overcome seasonal demand on the processing plant.

The overwhelming reason why mankind resorts to nature in these instances is that he does not have to pay for the reservoirs only access to them. Despite the usual inconvenience of location, the economic advantage predominates. It is not unreasonable to look for an answer to the problem of large scale energy storage by similarly turning to nature. In the long term, a possible solution might be the storage of pressurised hydrogen gas in underground reservoirs particularly the water bound ones known as aquifers. In relation to thermo-

chemical systems, the concept of storing mixtures of nitrogen and hydrogen in aquifers is particularly interesting as a method of storing solar energy.

In passing, we must emphasise that such a method of storing energy would, in the beginning, only be suitable for particular localities where there happened to be a natural reservoir in the vicinity. However, the method would become of general practicability as the scale of usage increased, as more areas were used for collection and as thermo-chemical energy transport lines grew and linked to form a regional grid.

3. Description. We will confine our attention to the aquifer as a potential storage reservoir. This is because aquifers are much more prevalent than other potential reservoirs such as salt domes (which must first be leached) and dis-used gas and oil wells (which are essentially aquifers in any case but with special problems and advantages).

Aquifers may be defined for our purposes as water bearing porous sedimentary formations comprising a permeable layer bounded above and perhaps below by an impermeable layer. We will refer to the upper impermeable layer as the cap layer. The topography of the under surface of the cap layer is of particular importance. Like the oil and gas explorer we would search for closed structures, that is ones which may be completely enclosed by a horizontal base plane. The dome is a particularly good example of a closed structure. In practice the closed structure is drilled and gas is pumped in so as to displace the water downwards in the permeable rock. Thus the horizontal plane alluded to above is in reality the gas water interface under the action of gravity. For a favourable reservoir we would want the closed structure to be such that it could be completely emptied of gas as the horizontal plane moved upwards. This requires a structure free of 'humps' and requires the drill to enter the top of the structure.

Access to the reservoir would be by standard lined well typically 20 cm diameter. It is assumed that a leak-tight joint can be made between the well lining and the impermeable cap layer.

The natural or discovery pressure of the water in an aquifer invariably depends on depth and is due to the hydrostatic head. A good estimate of pressure can be made on the basis of 1 atmosphere per 10 metres of depth. In order to displace water by gas, the gas pressure must exceed the natural pressure and in order to recover gas the gas pressure must be less than the natural pressure.

As gas is pumped into an aquifer, water is displaced and must be accommodated elsewhere. The vastness of sedimentary basins allows this displaced water to be accounted for by the compressibility of water and rock (for example the weight of mantle above the aquifer is supported partly by the permeable rock and partly by the ground water under pressure. A slight increase in water pressure therefore allows the permeable rock to expand and thus extra water can be accommodated not only as a result of the compressibility of water but also because of the increased volume of the rock.) Alternatively, the displaced water may travel towards the surface and affect the water table in some locality. Man-made outlets might consist of secondary wells connected to a surface water reservoir or there might be constructed a secondary underground air reservoir the compressibility of which allows accommodation of the displaced water. The man-made outlets would of course be disposed outside the closed structure to be employed as the energy reservoir.

As gas is introduced to a reservoir at a pressure above the natural pressure, water is displaced at a certain rate. Experience with natural gas storage demonstrates that aquifers behave over periods of months as constant pressure variable volume reservoirs and over periods of days as fixed volume variable pressure reservoirs. This is because of the relation between pressure gradient and the flow rate of ground water through the permeable layer.

The storage capacity of a closed structure depends not only on the gross volume but also the porosity and volume of connate water. The former is the fraction of void in the rock which might range up to 0.5, and the latter is the water which remains wetting the rock when the remainder of the water has been displaced by gas. The irreducible connate water may be just a few percent but increases with increasing porosity and decreasing permeability reaching 1.0 for the cap layer. A typical fine sand might have a permeability of 1000 m Darcy, a porosity of .25 and connate fraction of 0.1. The net storage volume would therefore be about .22 of the gross volume.

The immense storage capacity of aquifers may be illustrated by an example. Assume a closed dome structure consisting of a permeable layer 3 m deep and the gas extending to a radius of 300 m - from a geological point of view quite small. Such a structure would have a net volume of $1.8 \times 10^5 \text{ m}^3$ (with the porosity and connate water fraction stated above) and at a depth of 3000 m would store nitrogen and hydrogen with a calorific value of $6.8 \times 10^7 \text{ MJ}$ when converted to ammonia. At a conversion efficiency of 25% this represents 10 MJ continuous electrical generation for 20 days. This is about optimum for one well or bore.

Australia is well endowed with sedimentary basins as can be seen in Figure 2. Many of these basins are multilayered and extend to great depths.

As a result of exploration for oil and gas sedimentary basins are becoming well mapped and closed structures easier to distinguish and intersect. Figure 3 is an example of a contour map featuring several very large closed structures including the Gidgealpa field. The structures we are interested in are of much smaller scale and, I am assured by several geologists, correspondingly much more numerous.

4. Mechanisms for loss of hydrogen. There is no direct evidence that hydrogen gas will remain stored underground without rapidly leaking away. Hydrogen is known to escape through small cracks and even through solid walls where other gases would be unable so one might suspect that hydrogen would be a difficult gas to store underground. Natural gas generally contains nitrogen and very occasionally helium. We may infer therefore that it is possible to store these gases indefinitely. The fact that helium may be stored is important since, next to hydrogen, helium is also prone to escaping through the smallest crack. The absence of hydrogen in natural gas need not imply that hydrogen is difficult to store since it may be argued that any free hydrogen would have combined with other substances in the course of geological time. In any case the most likely origin of hydrogen in natural gas would be from organic material and therefore free hydrogen could only occur if such material were dissociated and the hydrogen and remaining carbon or hydrocarbon segregated. Apart from extreme heat it is difficult to imagine such a process. In the case of extreme heat the conditions for containment of hydrogen would be quite adverse but also quite different from those we are contemplating where liquid water is the prime sealant.

As far as this author is concerned a closed structure is essentially a vessel whose walls are of water: water held in connate form in the domed roof of the vessel, and displaceable ground water in the permeable formation forming the floor.

Such a view implies that every possible crevice in the cap layer contiguous with the permeable layer has been sealed with water during the eons in which the cap layer has been in contact with ground water or from the time that the individual particles of the layer were first laid down as a sediment under water. The veracity of this view, which

may be called the water wall hypothesis, can be demonstrated finally only through research.

Accepting then the water wall hypothesis, an obvious mechanism of loss is by diffusion and solution of gas in water. This will not be complicated by convection currents in the water, at least in the static case, because of the cellular matrix in which the water resides so that simple diffusion theory should suffice.

Precise figures for solubility and diffusion coefficient of nitrogen and hydrogen are not known for the conditions encountered in the ground water. However, by extrapolation of known data using Henry's law we arrive at the following figures for solubility at 80°C and 300 ats pressure:

Nitrogen	12×10^{-4} mole fraction
Hydrogen	20×10^{-4} mole fraction

The density of dissolved nitrogen and hydrogen in water is therefore approximately 1% of the density of gas alone at 300 ats.

The diffusion coefficient of both nitrogen and hydrogen in water under the conditions of interest is thought to be of the order of $10^{-4} \text{ cm}^2/\text{s}$. The corresponding times to penetrate specific distances are:

x	t
1 cm	10^4 S. (3 hours)
10 cm	10^6 S.
1 m	10^8 S. (3 years)

It follows that after three years the loss of gas, reckoning on the solubility and diffusion mechanisms only, would be equivalent to the walls moving out 1 cm and a layer of compressed gas 1 cm thick being trapped.

Diffusion may be complicated by surface diffusion effects but preliminary enquiries suggest that this will not be significant.

Simple diffusion is therefore not likely to be a problem and in any case the losses from this cause are not cumulative. Perhaps a more serious mechanism is associated with the cycling of the reservoir from full to empty. As the reservoir is filled with gas the receding ground water leaves behind wet porous rock. The connate water will rapidly become saturated with dissolved gas and, for a connate water fraction of 0.1, the dissolved gas will amount to 0.1% of the stored gas provided there are no extraordinary surface effects enhancing solubility. As the reservoir empties and unsaturated ground water replaces gas, presumably the dissolved gas in the connate water will diffuse out and will be carried away when next the reservoir fills with gas.

However, a counter argument suggests that loss due to cycling will be much less than indicated above. Briefly it is that as the reservoir fills with gas the connate water will be left already saturated because the last contact each element of connate water has with the receding ground water is with the saturated surface layer. None of the newly stored gas is therefore lost by diffusion into the connate water.

5. Power capacity of well. The capacity of a well connecting a gas reservoir depends on the allowable flow rate into or out of the well. One of the limitations to flow rate is friction pressure drop. The allowable friction pressure drop depends on the ratio of the power loss through friction to the power being transmitted as the chemical energy of the flowing gas. If we assume that the allowable friction power is 7% of the electrical power ultimately derived from the chemical energy of the flowing nitrogen-hydrogen gas, it can be shown that the friction pressure drop must be limited to 17% of the nominal system pressure. If the latter is 300 ats then friction must be no greater than 50 ats.

Let us first assume that friction is predominantly due to flow along the wall liner. It can be shown that for a 20 cm diameter liner 3000 m long a flow of approximately $0.45 \text{ m}^3 \text{ s}^{-1}$ corresponds to a pressure drop of 50 ats.

A second cause of friction will be through the permeable sedimentary layer. Pressure drop here will depend on the permeability of the medium, the depth of drilling into the medium and the diameter of the drilling (which may conceivably be larger than the well diameter). As an example we present the results for permeability of 1000 m Darcy (a fine sand), a drill depth of 1 m and diameter 20 cm. A flow of $1.5 \text{ m}^3 \text{ s}^{-1}$ corresponds to a pressure drop of approximately 50 ats.

Apart from friction, a further limitation to flow is particle entrainment. Obviously this applies only to flows out of the well and moreover, is of a transient nature since presumably, as particles are removed the likelihood of further particles being broken off is reduced. The particle lifting capacity of a fluid depends on $V^2 \rho_f$ where V is the fluid velocity in m s^{-1} and ρ_f is the relative density of the fluid (water = 1). Rock particles of 1 mm diameter can be lifted with $V^2 \rho_f \geq .05$, of 10 cm diameter with $V^2 \rho_f \geq 5$. Experience with natural gas and artesian wells suggests a practical limit to $V^2 \rho_f$ of about 2.5 which indicates that particles of such a size as to actually block the flow are the ones of real concern, smaller ones being simply removed in settling tanks on the surface. Thus, based on $V^2 \rho_f = 2.5$ we arrive at a maximum outflow at 300 ats of $.16 \text{ m}^3 \text{ s}^{-1}$.

It is now necessary to relate these maximum flow rates into and out of storage to an electric power base load and for this purpose we refer to Figure 4. If we call the base electric power E , a continuous thermal power of $4 E$ will be required assuming 25% conversion efficiency. However, because of the intermittent nature of solar energy we can count on only 0.25 for the

capacity factor of the collectors which implies a peak thermal power from the collectors of 16 E. It follows that the maximum energy inflow to storage will be 12 E and out of storage 4 E. We may now relate 12 E to the flow limit of $0.45 \text{ m}^3 \text{ s}^{-1}$ due to liner friction drop or alternatively 4 E to $0.16 \text{ m}^3 \text{ s}^{-1}$ being the assumed particle entrainment limit. Of the two the former is the lower limit and can be shown to give

$$E = 13.5 \text{ MW}_e$$

Larger well diameters will of course give higher values.

6. Cost of storage. A summary of costs as presently estimated are shown in Figure 5. These estimates are for underground storage of nitrogen and hydrogen, surface pressure vessel storage of the same gas mixture and 1 atm refrigerated storage of liquid ammonia. In each case only the cost of the storage facility is included and not the cost of the stored substance. A surprising result is the short storage time above which the underground storage of gas is actually cheaper than the above ground storage of liquid. If this trend is borne out by further work it would imply that thermochemical systems based on gas-gas reactions may be preferable to ones based on gas-liquid reactions.

7. Contamination. After storage underground, it is expected that recovered gas will be contaminated with impurities picked up from the ground water and rocks. These contaminants will in most cases have to be removed because of their poisonous effect on the catalysts. The magnitude of this task may be brought into perspective by considering the following examples of modern practice.

a. ammonia and methanol synthesisers operate on synthesis gas derived from naturally occurring hydrocarbons, including gases, which have been

extracted from reservoirs in a contaminated state. There is no doubt therefore that technology exists capable of removing any contamination of stored nitrogen and hydrogen to a degree acceptable to the catalysts.

b. At Gidgealpa raw gas is processed ready for market and then stored underground. Presumably the gas extracted from storage is of better quality than the original raw gas despite contamination during subsequent storage. The implication is that this contamination has been found to be small.

It is worth making the point that contamination is subject to the same sort of mechanisms as we have considered for loss of stored gas viz by diffusion out of solution of ground water. It might be expected therefore to be of the same magnitude, to be storage time dependent and to diminish as time goes on because of the gradual depletion of contaminants in the ground water associated with the storage reservoir. The rate at which new contaminants are introduced into the region is slow because typical natural ground water velocities are less than 1 m/yr.

8. Conclusion. Clearly there are many unanswered questions which can only be attacked through a comprehensive programme of research. However, the discussion presented here indicates that there is an 'a priori' case for pursuing such a programme because the losses appear to be of tolerable magnitude, the costs to be less than any other form of large scale storage, and the technical problems to be manageable. The costs and capacities of reservoirs given here have been for nitrogen and hydrogen. When hydrogen alone is considered both costs and capacities improve giving added value to research carried out in this area.

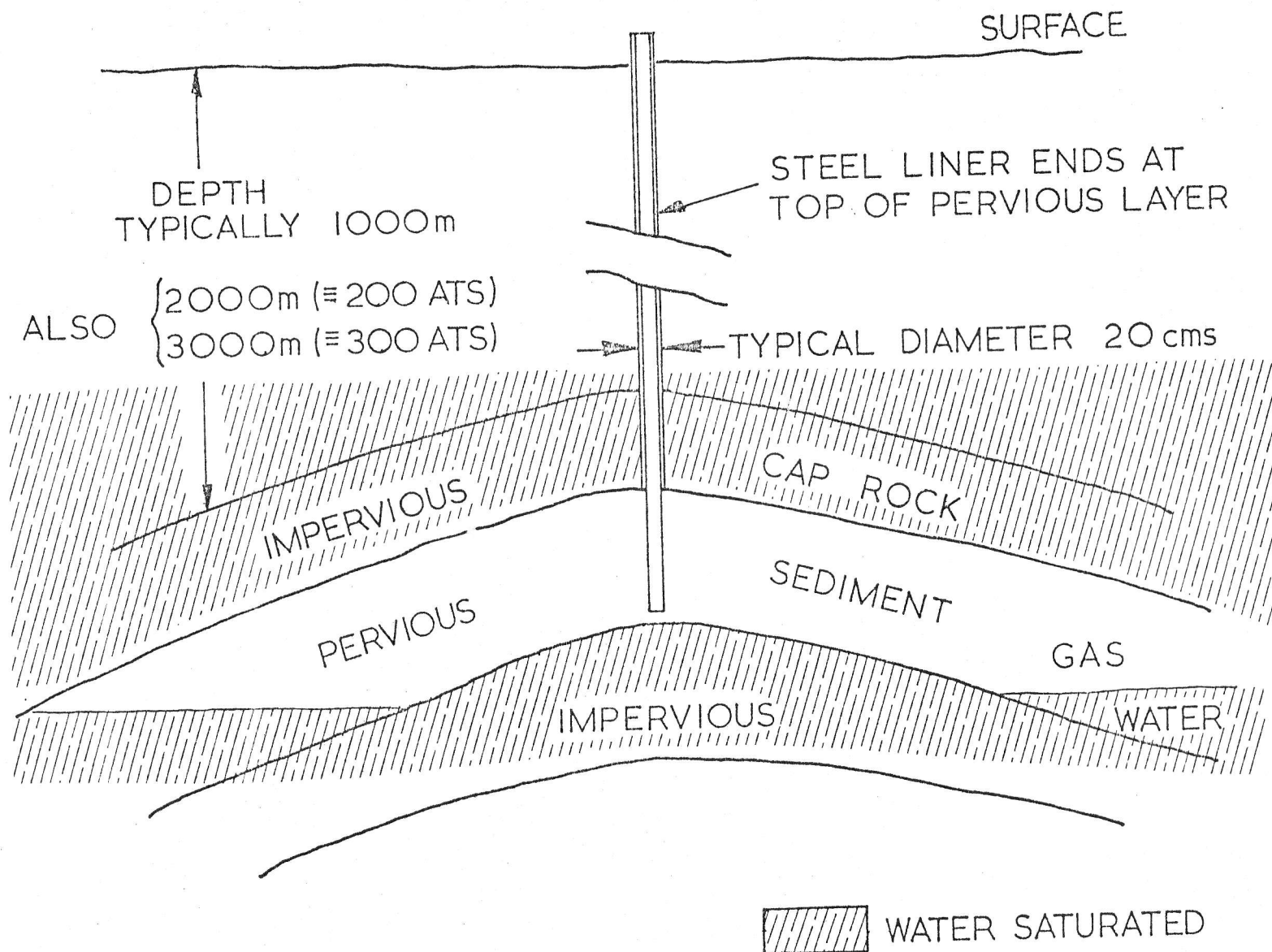


fig. 1

Section of an aquifer storage reservoir

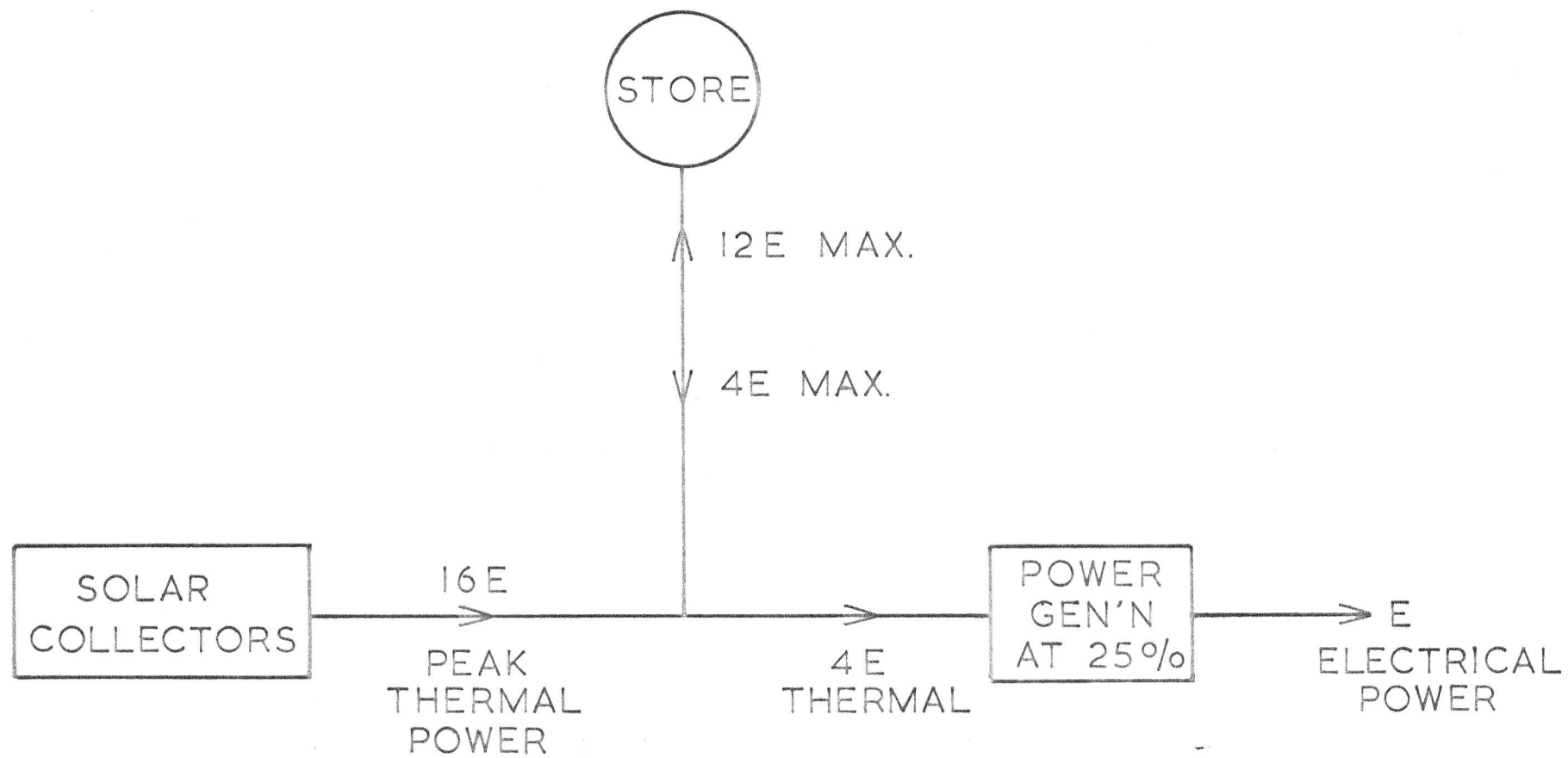
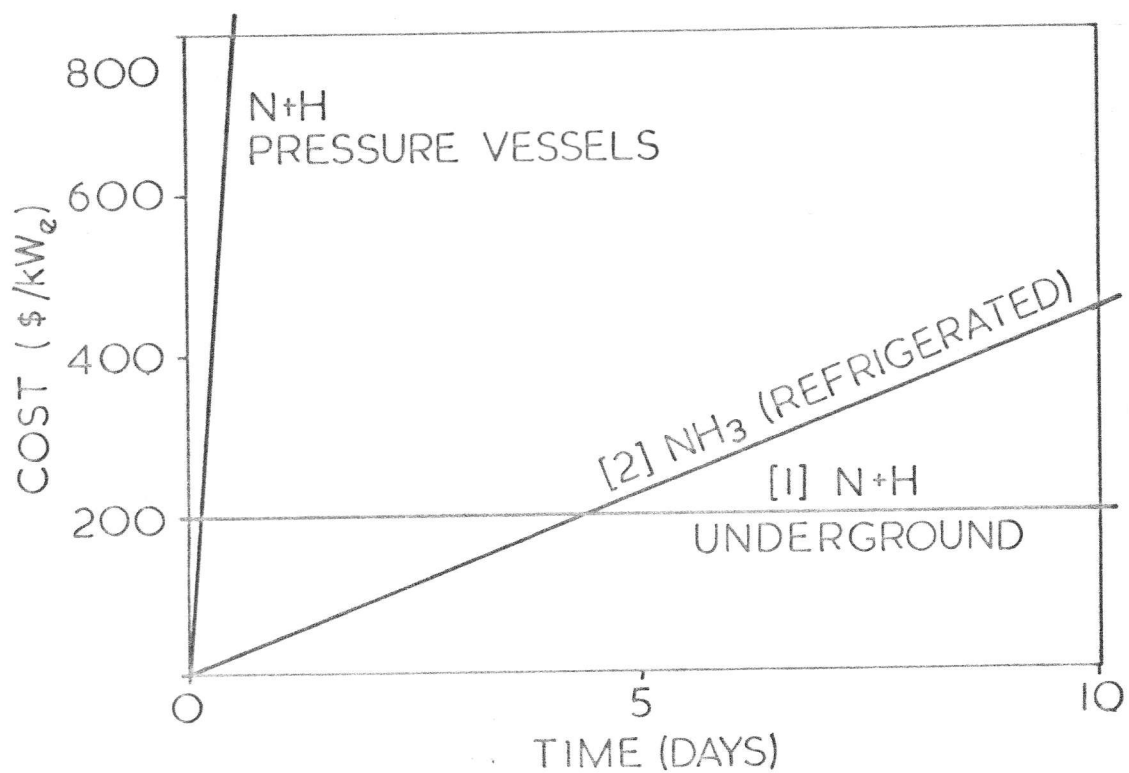


fig. 4.



[1] BASIS 15MW_e (Continuous) per bore
 Drilling & contaminant removal } \$3M per bore

[2] ICI known installation \$2.2M for 5000 T

fig.5

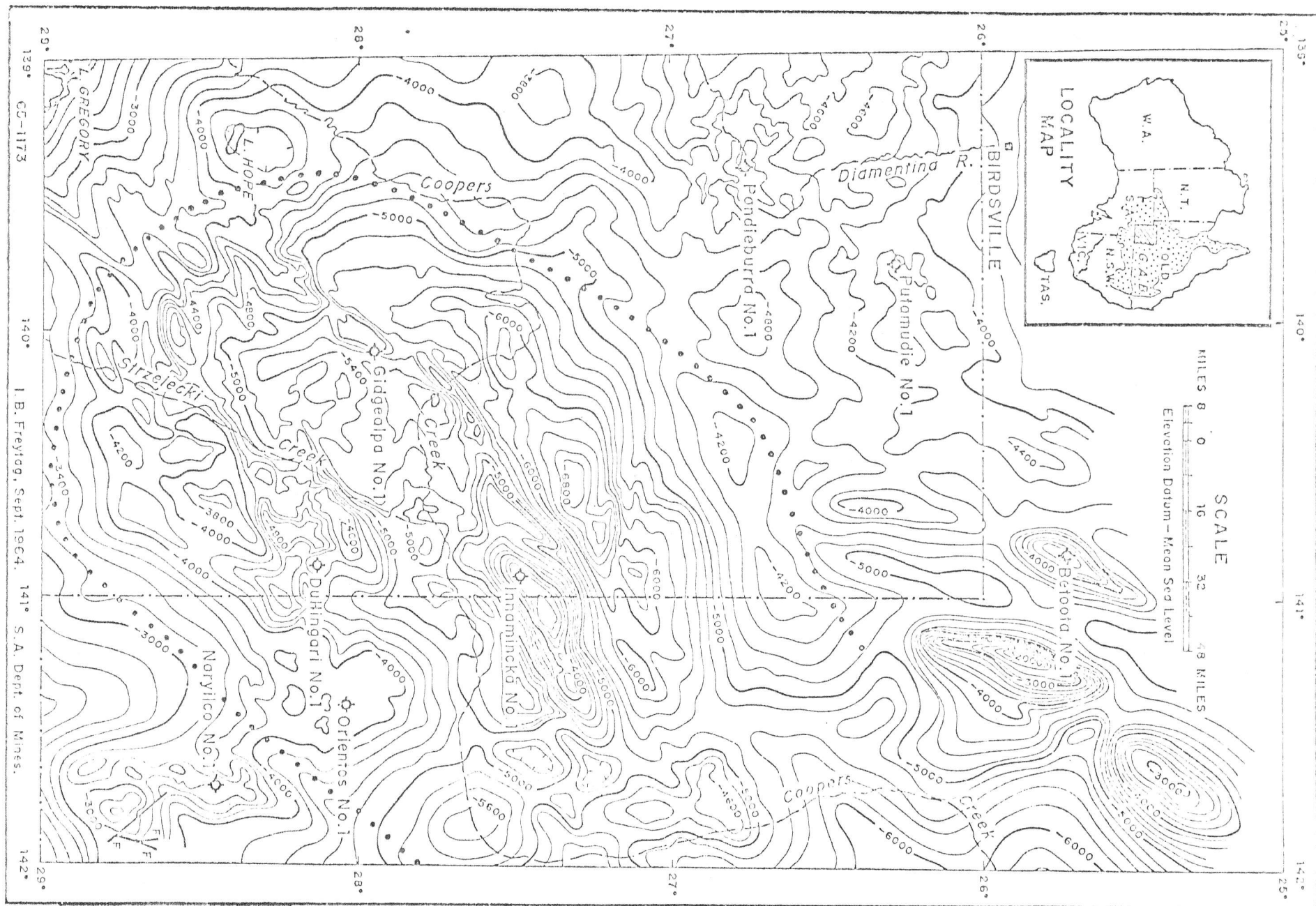


fig. 3

STRUCTURE CONTOUR MAP OF PORTION OF THE GREAT ARTESIAN BASIN OF AUSTRALIA;
DATUM: APPROXIMATE TOP OF LOWER CRETACEOUS TRANSITION BEDS