Feasibility analysis of using salt caverns for storage of redox flow batteries

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Abstract: Renewable energy holds significant promise of replacing the conventional energy sources. However, the wind and solar energy exhibit the obvious discontinuity, instability, and uncontrollability problems. Redox flow batteries are a novel energy technology, whose most appealing features are high efficiency, long life, and reduced environmental impact. Salt rock has low porosity and permeability, and can self-heal from damage. A salt chamber after water-dissolution is considered as an excellent geological body for energy storage. This study reviews in detail the current worldwide status of salt cavern utilization. Drawing on the salt-carven oil and gas storage technology, the feasibility of storing electrolytes in salt caverns is analyzed considering the physical characteristics of salt rock deposits, and economic and environmental factors. Two medium salt caverns in Jiangsu Province were selected and used as a case study for storage for the all-vanadium flow batteries. The working principle of salt cavern is introduced, and the efficiency of energy storage of the entire system is approximately calculated. Based on the assessment of the existing salt caverns in China, it has been found that using salt caves for electrolyte storage can solve the current problems of disposing old battery electrolyte.

1. Introduction
To reduce the negative impact of environmental pollution and the risk of climate change caused by the consumption of fossil fuels, the development of renewable energy sources to replace the traditional ones, and the transition to a clean-energy economy are essential. Solar and wind energy are the most promising alternatives with many applications utilizing photovoltaic panels and wind turbines [1]. However, wind and solar energy sources are highly intermittent, and, therefore, require energy storage to guarantee continuous supply of energy. An overview of China's abandoned electricity from 2016 to 2018 is shown in Figure 1.
Energy storage systems have been in development for long time to reach their present mature state, including the compressed-air energy storage (CAES), pumped-hydroelectric storage (PHS), and electrical-energy storage (EES). In designing superior storage technologies, the following characteristics should be considered: scalability/power bridging, fast response time, high storage capacity, low cost, high efficiency, long life, and low environmental repercussions [2]. The CAES and PHS are largely limited by geological factors, so they cannot be widely used worldwide. Emerging storage technologies, such as the redox flow battery (RFB), hope to achieve the above requirements. The RFB is a type of energy storage device capable of providing reversible conversion between electrical and chemical energy. Compared to other storage technologies, power conversion is separated from energy storage, thus allowing for independent power and energy sizing. This feature allows for virtually unlimited capacity, simply by using larger storage tanks.

Salt caverns are large underground open spaces created by controlled water leaching in a salt formation. The characteristics of salt rock, such as isotropic mechanical properties, low permeability, and solubility in water, make it an ideal medium for energy storage [3,4]. Their volume is typically $10^3$-$10^6$ m$^3$. At present, they have been used for storing multiple media. Based on the existing technologies, utilizing salt caverns as electrolyte storage in a similar way would promote the development of clean energy, and, simultaneously, save large amounts of manpower and material resources. In recent years, research on the salt-cave energy-storage battery systems has been carried out. Ewe Gasspeicher GmbH is building a RFB in underground salt caverns with enough output to supply a day's worth of power to 75,000 homes, giving the battery a capacity of up to 700 MWh and output of up to 120 MW, respectively. Such a technology will further address the grid integration problem of renewable energy.

This paper reviews the current status of the development of salt-cave storage, and evaluates the feasibility of building salt caverns as electrolyte reservoirs for RFBs. Furthermore, we selected a case study for analysis, and found the potential to be significant. The results can be used to guide the construction and production of salt caves as electrolyte reservoirs.

2. Status of salt cavern utilization
Using salt caverns to store oil and natural gas, etc., has a long history. As early as in 1940, Canada was the first country to envisage storing liquids and gases in salt caverns. However, the idea was first
realized by Britain, which stored crude oil in salt caverns during the Suez Canal crisis in the 1950s [5]. The world's first salt-cave gas storage was built in the Soviet Union in 1959. Subsequently, the United States, Canada, and other countries have successively built salt-cavern gas storage. The working principle of salt-cavern gas storage is that after the natural gas is injected into the salt cavern, the pressure difference is used for injection and production. Due to its high injection-production rate and low levels of cushion gas, this technology is widely popular all over the world.

Construction of the Jintan gas storage, the first salt-cavern gas storage in China, started in 2004, and it was officially opened for use in 2007. The cumulative gas production has exceeded 2.4 billion m³. For strategic reserves, salt caverns can also be used to store petroleum. Unlike gas storage, petroleum storage exhibits small pressure fluctuations and uses large casing sizes. Due to the difference in density, the replacement of saturated brine can realize the injection and production of stored materials. According to incomplete statistics, about 40% of the German oil reserves are stored in underground salt caves. Moreover, methods utilizing compressed air and hydrogen in salt caverns can also be used for large-scale energy storage applications. The Huntorf plant, located in North Germany, was commissioned in 1978 as the world’s first compressed air energy storage, has been successfully running for more than 30 years.

3. Feasibility analysis of building salt caverns as electrolyte storage

3.1 Basic features

China's underground salt mines are rich in reserves and have a wide distribution range, the total volume has reached 2.5×10⁶ m³, while the volume of newly dissolved chambers grows by 5×10⁶ m³ annually, but the utilization rate is only 0.2%. Salt rock is a product of natural geological processes, the crystal form is uniaxial, mainly composed of NaCl and a small amount of impurities, is soluble in water, and its color is mostly white or light red. It has low strength of a typical soft rock, and the uniaxial compressive strength is 13.3-33.6 MPa, while the uniaxial tensile strength is 1.10-2.61 MPa, respectively. Due to its composition, the salt rock will not react chemically with any stored electrolyte. There are different numbers of salt mines distributed worldwide, most of them is concentrated in 500-1500 m. The originally deposited salt rock has a very dense structure with very small porosity, generally less than 1%. Sutherland and Cave [6] studied the changes in permeability of WIPP salt rock with hydrostatic pressure and time, and concluded that if this formation is in a state of hydrostatic compression in its undisturbed state, then its in-situ permeability is less than 5×10⁻²⁰ m³. Furthermore, the introduction of non-lithostatic stress states into the formation may produce an increase in permeability of the formation. However, this increase in permeability will probably be reversed after the formation returns to a hydrostatic pressure state. Different from the irreversible influence of other rocks in the excavation process, salt rock has obvious advantages when used as a storage for electrolyte.

3.2 Stability evaluation

Good airtightness is the prerequisite for a deep underground chamber as an electrolyte storage for flow batteries. A salt cavern will inevitably be disturbed during excavation or drilling to produce expansive micro-cracks, and electrolyte will leak if these micro-cracks cannot heal, causing severe environmental damage. The self-healing properties of the salt rock can ensure the stability of the salt cave, while the damage self-healing characteristics manifest macroscopically as strengthening of the mechanical properties of the overall structure, and microscopically as microcrack closure, crystal growth, and crack filling. Jie et al. [7] analyzed the self-healing capacity of damaged salt rock with different initial damage, and found that when the damage degree is below a certain threshold, the self-healing ratio of rock salt increased with the increase in damage intensity. Yin et al. [8] conducted a self-healing study on the salt rock after uniaxial compression, and found that the permeability decreases significantly as a
result of repair, and can be comparable to that of the initial state. These studies can provide evidential support for predicting the stability of deep salt rocks when storing electrolytes.

3.3 Economic evaluation
At present, salt caverns are mainly formed by using the water-dissolution method. Fresh salt water is injected into the underground salt-rock layer, and brine is extracted after the salt rock is dissolved in the water. Compared with other caves where electrolyte can be stored, the cost of cavity creation is lower. Brines produced during cavity-making can be used to produce high-purity salts, which find industrial applications. The cavity formed after salt extraction can be used to store the electrolyte of the flow battery, which avoids the expensive design and processing of storage batteries for flow-battery electrolytes. The project will not cause pollution of groundwater, because of the salt cavern has good airtightness. After the life of the flow battery is over, it can be recovered using an injection pump. In addition, because the electrolyte is stored underground, the required personnel requirements and power consumption are much less than on the ground. Due to the significant capacity of the built electrolyte storage, it can successfully complete the functions of peak shaving and power storage, thus, its economic potential is vast.

3.4 Electrolyte
The salt-cavern flow-battery system is based on the RFB. The development of the electrolyte directly determines whether the salt cavern can replace the tank as a medium for storing electrolyte. According to the type of electrolyte in flow batteries, they can be divided into aqueous and non-aqueous systems. Aqueous electrolytes use water, or inorganic acids and bases as supporting electrolytes, whereas non-aqueous electrolytes use organic solvents in supporting electrolytes. All-vanadium, the bromine-polysulfide, and the zinc-bromine flow batteries have achieved certain commercial maturity [9]. The VRFB uses redox-couple reactions in both the positive and negative half-cells to minimize cross-contamination, thus, it has received widespread attention. It capitalizes on four different oxidation states of vanadium ions to form two redox couples separated as the anolyte and the catholyte with only one active element in both sides [10]. The redox reactions occurring in the VRFB are given below:
At the positive electrode: \( VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \)
At the negative electrode: \( V^{3+} + e^- \rightleftharpoons V^{2+} \)
Over cell reaction: \( VO_2^+ + V^{2+} + 2H^+ \rightleftharpoons VO^{2+} + V^{3+} + H_2O \)
Non-aqueous RFBs have recently developed rapidly, achieving higher electrochemical windows and higher energy density. They use organic substances instead of water as the solvent of the flow battery. Through screening or mixing of organic solvents with different properties, the working range of a flow battery can be expanded, and the wide application of the flow batteries can be realized. Liu et al. [11] investigated the electrochemistry of a single-component RFB employing vanadium(ill) acetylacetonate in acetonitrile and tetraethylammonium tetrafluoroborate. Brushett et al. [12] proposed a non-aqueous lithium-ion RFB. Chai et al. [13] designed two viologen analogues with poly-tails as anolytes for non-aqueous. However, since there is no suitable membrane with high ion conductivity and high selective permeability, non-aqueous flow batteries are currently only in the laboratory stage, and have not yet been commercialized, thus, they are not considered in this research.

4. Case study
The Jintan Salt Mine is one of the four major salt mines in Jiangsu Province, with total reserves in excess of 12.5 billion tons. Located in the Golden Triangle of the Lower Yangtze River in the East China Economic Zone, one of the most economically developed regions in China, annual electricity consumption of the region is extremely high. Two medium-sized salt caverns were selected in this area as case studies in this paper.
4.1 Geological conditions
The salt system of the Jintan Salt Mine belongs to the middle and late Pliocene deposits of the Early Tertiary. The salt system strata can be divided into three layers from top to bottom. These are gypsum mudstone layer above salt, salt rock layer, and gypsum mudstone layer below salt. The salt rock layer is dominated by mud-bearing salt rock and gray salt rock, and salt content is generally higher than 85%. In addition, the burial depth is generally 800-1300 m. The upper covering layer and the underlying floor are composed of tight rock layers, such as mudstone and gypsum rock, with good sealing performance. Several salt caverns for gas storage have been constructed in this area, and a compressed-air storage station is under construction.

4.2 System design
The proposed system is composed of pumps, electrode material, electrolyte, membrane, and two electrolyte reservoirs. When in the energy storage stage, the circulation pump is started, the electrolyte in the flow-battery stack is injected into the salt cavern, and the same amount of electrolyte in the chamber is replaced to enter the flow-battery stack for recharging. In the power generation stage, the electrolyte in the flow-battery cell stack generates electricity through a redox reaction. When the electrolyte reaction is nearly completed, the circulating pump is driven by the residual power of the flow-battery stack to inject the electrolyte of the flow-battery stack into the dissolution chamber, replacing the same amount of electrolyte, and discharging again. The system schematic diagram is shown in Figure 2.

![Figure 2. Schematic diagram of salt caverns as storage for RFB](image)

The RFB capacity depends on the volume and concentration of the electrolyte solution. The all-vanadium RFB is considered in this research, which uses vanadium dissolved in aqueous sulfuric acid. This offers an advantage of using the same metal ions in both electrolytes, and avoiding the electrolyte pollution caused by the cross-linking of ions. All-vanadium flow-battery energy storage system mainly includes an all-vanadium flow cell battery system, battery management system, power conversion system, and transformer and energy management system. Two medium salt caves with a size of 1×10^5 m^3 were selected in this research; the remaining design parameters are shown in Table 1.

| Name         | Parameter     |
|--------------|---------------|
| Membrane     | Nafion 212    |
| Electrode    | Graphite felt |
| Electrolyte  | H₂SO₄ + Vⁿ⁺   |
| Temperature  | 25°C          |
4.3 System performance
Due to the instability of renewable energy input, the entire system consists of 2500 individually regulated unit energy storage systems. Under the unified scheduling of energy management, any number of individual unit energy storage systems can be selected to start according to the amount of renewable energy generation, which underpins the reliability of the system operation. The rated output power of a unit energy storage system is 1 MW. According to the above parameters, the total capacity of the system can reach 2500 MWh. Zeng et al. [14] studied VRFBs for large-scale energy storage, and found that an efficiency of 80.3% can be achieved. However, due to the longer pipeline, more hydraulic-friction loss and pipeline-friction loss will be caused, and the actual efficiency will be less than 80.3%.

5. Conclusions
The salt-cavern flow-battery energy-storage system has the advantages of large energy storage capacity, fast corresponding speed, and flexible peak shaving. It can help to solve the problem of large-scale grid integration of renewable energy. Local geological conditions are the most criterial consideration for the proposed system, and the characteristics of the Jintan Salt Mine are favorable for storing electrolytes of a RFB. With the increasing maturity of salt-cavern storage technology, the salt-cave flow-battery systems will also develop rapidly, which is of great significance for renewable energy to be able to replace gradually traditional fossil energy.
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