Mechanism of groundwater inrush hazard caused by solution mining in multilayer rock salt mine area: a case study in Tongbai County, China

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ABSTRACT

The solution mining of salt mineral resources may contaminate groundwater and lead to water inrush out of the ground due to brine leakage. Taking a serious groundwater inrush hazard in a large salt mining area with three different types of ore beds which are trona (trisodium hydrogendicarbonate dihydrate, also sodium sesquicarbonate dihydrate, Na$_2$CO$_3$·NaHCO$_3$·2H$_2$O, is a non-marine evaporite mineral), glauber (sodium sulfate, is the inorganic compound with formula Na$_2$SO$_4$ as well as several related hydrates) and gypsum (a soft sulfate mineral composed of calcium sulfate dihydrate, with the chemical formula CaSO$_4$·2H$_2$O) in Tongbai County of China as an example, this paper mainly aims to analyse the source and channel of the inrush water. Based on the understanding of geological and hydrogeological conditions, the study obtained hydrochemical data of groundwater at different points and depths first; and then analysed the pollution source and pollutant component from single or mixed brines by both physical-chemical reaction principle analysis and hydrogeochemistry simulation method; finally possible leakage brine conducting channel to the ground had been discussed from both geological and artificial aspects. The results reveal that the brine from the trona mine is the major pollution source; the fissure zone in NW-SE direction controlled by the geological structure provides the main channels for the leakage brine to flow into the aquifer around the water inrush regions, and a large number of waste gypsum exploration boreholes are the channels that supply the polluted groundwater inrush out of the ground. The research can offer a valuable reference for avoiding and assessing groundwater inrush hazard in similar rock salt mining area, which is advantageous for both groundwater quality protection and resident health.
1. Introduction

Solution mining is commonly used in salt mine exploitation, as salts are soluble in water. In this method, high-pressure and -temperature water with low salinity is injected into a mineral deposit through production wells to dissolve the mineral salts. After being transported out of the wells, the soluble salt is purified and further processed. However, the high-pressure and -temperature water used in this process not only dissolves minerals but also may cause fracture of strata, which usually results in hazards such as brine leakage or groundwater inrush. So that underground drinking water for residents is normally polluted after the groundwater inrush hazard, and make threaten to the health of local people.

Many scholars (Clark and Fritz, 1997; Liu et al., 2015; Wu et al., 2016) have studied the case of groundwater inrush hazards in both coal and metal mines, and some adopted methods are as follow: the use of water level/temperature criterion (Yuan and Gui, 2005; Ma and Qian, 2014), stochastic simulation (Fernandez-Galvez et al., 2007), numerical simulation (Liu et al., 2009; Kang et al., 2012; Shao et al., 2013; Houben, et al., 2017), water chemical analysis (Robins, 2002; Fernandez et al., 2005; Hu et al., 2010; Cobbina et al., 2015; Lee et al., 2016; LeDoux et al., 2016) (isotope analysis, water quality type correlation analysis), multivariate statistics (Chen and Li, 2009; Lu, 2012)(discriminant analysis, clustering analysis), fractional advection dispersion equations (Ramadas et al., 2015) and nonlinear analysis (Hao et al., 2010; Gao, 2012) (fuzzy mathematics, grey correlation analysis, etc.).
However, due to the particularity of mining method (solution mining) and complex chemical-physical reactions during mining process (under high-pressure and -temperature), research about solution mining is more focusing on mining techniques (Jiang and Jiang, 2004; Kotwica, 2008; Namin et al., 2009), mining cavity stability analysis and sinkhole problem (Staudtmeister and Rokahr, 1997; Bonetto et al., 2008; Ezersky et al., 2009; Goldscheider and Bechtel, 2009; Closson and Abou Karaki, 2009; Vigna et al., 2010; Frumkin et al., 2011; Ezersky and Frumkin, 2013; Qiu, 2011; Blachowski et al., 2014), and geohazards especially in karst area due to human-induced underground caves (Waltham and Fookes 2003; Parise and Gunn 2007; Zhou and Beck 2011; Parise and Lollino 2011; Lollino et al., 2013; Gutierrez et al., 2014; Parise et al., 2015), but rarely on the source and channel analysis of inrush water in solution mining accident.

The studied rock salt mine area is located in Tongbai County of Henan province in China. This mine area has the second largest trona reserves worldwide, while its glauber salt reserves reaches 45 million tons. Since trona and glauber salt had been put into production in 1990 with single and double well convection mining as their main producing method, from June 2011 to May 2013, five inrush points appeared in Anpeng Town of Tongbai County. Among these five inrush points, four (Y1~Y4) were long-term (more than 2 years) inrush points with stable discharge, while one (Y-5) was a sudden inrush point (as shown in Fig. 1 and Fig. 3). On 1 February, 2013, almost 200 m$^3$ of mud and sediment erupted out of the ground at Y-5 point. The area of inrush point was almost 4 m$^2$; the average water
inflow was 20-30 m$^3$/d while the largest inflow reached 200 m$^3$/d, and the water inrush lasted for approximately 3 months. During the Y-5 inrush accident, according to the field investigation, a trona production well named “S02”, which is 200 m away from the inrush point, was broken at the depth of 234 m for a long period of time, and it was repaired on 15 March, 2013. During the whole water inrush process, the inrush groundwater led to the phenomenon of salinization at the house bottom in many villagers, and made water in many resident wells undrinkable any more.

Since the groundwater inrush hazard involving a wide range and the inrush source is quite hard to distinguish due to the multi-layer distribution of different ore body and complex of inrush water component. Therefore, in order to put forward a targeted treatment program to stop the water inrush as soon as possible, and mitigate the groundwater pollution in research region, the source and channel of inrush water were taken as the research emphasis in this paper. Furthermore, the research can offer a valuable reference for avoiding and assessing groundwater inrush hazard in similar rock salt mining area, which is advantageous for both groundwater quality protection and resident health.

2. Geological and hydrogeological setting

2.1. Geological conditions

The mining area is located in northwest of Tongbai County. The landscape is characterized by hollows and ridges, and has an elevation ranging between 140 and 200 m. Information about the strata, lithology, aquifer, and position of different ore beds in research area (Shi et al., 2013) are shown in Fig.
According to the field investigation, in the mining area, some buried faults develop in the Hetaoyuan Formation, but these faults have only small effect on the ore bed because they are either outside of the ore bed or distribute in a limited area.

### 2.2. Hydrogeological conditions

The groundwater in the mining area can be divided into pore water in the loose rock mass and bedrock fissure water according to lithology and hydrogeological features. In the upper part of Liaozhuang Formation, mudstone interbedded with gypsum is considered as the aquiclude. The shallow aquifer is an unconsolidated pore water aquifer located above the aquiclude, while the deep aquifer is a bedrock fissure aquifer located under the aquiclude. The water inflow of a single well with poor water content is approximately 100 m$^3$/d, while it can reach 1000-2000 m$^3$/d with rich water content. The annual variation of groundwater level is 2-4 m, while the depth is stable at 2.3-4 m. Residents in Anpeng Town take groundwater as source of drinking water, which comes from the well and belongs to porous aquifer.

As shown in Fig. 2, gypsum mainly exists on the top of the Liaozhuang Formation, glauber salt exists in the third member of the Hetaoyuan Formation, and trona exists at the bottom of the second member of the Hetaoyuan Formation and on top of the first member of the Hetaoyuan Formation. The surrounding rocks of every mineral layer include mudstone, shale, psammitic rock and dolomite,
which have sufficient thickness and good water-resistance ability. Therefore, the effect of groundwater on the mineral deposit is minimal in the mining area.

2.3 Distribution and characteristics of the ore body

The three ore bodies overlap in plane distribution, as shown in Fig. 3. The vertical distribution of ore bodies from deep to shallow is trona (buried depth: 1560.92-2929.53 m), glauber salt (buried depth: 1003.66-1397.58 m) and gypsum (buried depth: 134-338 m). Trona and glauber salt are at least 250 m apart from each other vertically.

Trona has 11 horizontal layers, with an average thickness of 2.11 m. The chemical composition of trona is mainly NaHCO₃ (average of 77.06%) and Na₂CO₃ (average of 16.33%) (Wang, 1987).

Glauber salt has 4 layers, with an average thickness of 8.93 m. The dip angle of ore bed layer is within 10°. The average mineral grade is 60.14%. The main composition of glauber salt is Na₂SO₄ (>90%), and with a small amount of NaCl.

3. Methods

Based on the field investigation result, the chemical characteristic analysis of inrush water in different sites and time, and analysis of physical and chemical reaction principle for different brines, combined with PHREEQC simulation method were adopted to judge the source of inrush water.

3.1. Sampling and test

The 5 groundwater inrush points (Y1~Y5) and some shallow groundwater points (resident wells:
SY1~SY6) nearby the accident site were chosen as groundwater quality sampling points, as shown in Fig. 3. Water from each point was sampled on 9 March, 2013.

Water samples were filtered by 0.45 μm millipore filtration membrane in the field, and then filled with a polyethylene bottle which had been soaked in acid and washed with deionized water. Filtered water samples were acidized until pH<2 by addition of ultra-pure HNO₃ for the determination of cation; water samples for the determination of anion would not be treated.

Elements tested in laboratory include 26 cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, Sr²⁺, etc.) and 5 anions (F⁻, Cl⁻, NO₃⁻, SO₄²⁻, NO₂⁻). The instrument for the determination of cation is inductively coupled plasma atomic emission spectrometer (Agilent ICP-OES 5100), while the minimum detection limit is 0.0001 mg/L; the instrument for the determination of anion is ion chromatograph (ICS-1100), while the minimum detection limit is 0.001 mg/L. CO₃²⁻ and HCO₃⁻ were tested according to “Groundwater quality test method: Determination of carbonate and bicarbonate by hydroxide titration (DZ/T 0064.49-93)”, while the minimum detection limit is 0.01 mg/L.

In addition, from March to April 2013, at Y-5 and Y-3 points, three water quality automatic recorders (Levelogger gold, Canada) were arranged for the inrush water monitoring. Monitoring indicators were temperature, water level and electrical conductivity. The monitoring purpose was to master the inrush water quality during the whole accident, especially in the process of well reparation.
3.2. Analysis on physical and chemical reaction principle in different brine mixing conditions

During the accident, the leakage brine of trona (2000 m below the ground) or glauber salt mine (1000 m below the ground) might flow through the gypsum deposit (200-400 m below the ground, comprising primarily CaSO₄) and caused physical and chemical reactions while inrush out of the ground. So the formation of inrush water chemistry component might be by glauber brine, or trona brine, or a mixture of the two brines flowed through the gypsum layer with physical and chemical reaction. To provide the basis for further analysis of the inrush water source, the physical solubility of gypsum, the reaction when glauber salt brine, trona brine, mixture of trona and glauber salt brine flow through the gypsum deposits were analysed.

3.2.1. The physical solubility of gypsum (CaSO₄)

Gypsum is slightly soluble; when in water, its acidity is apparent. Eq. (1) gives the dissolution rate equation of gypsum in water:

\[ R_{Gypsum} = k_1 \times \frac{A_g}{V} \left(1 - \frac{IAP}{K_{Gypsum}}\right) \]  

\[ R_{Gypsum} \] is the dissolution rate of gypsum; \( k_1 \): rate constant; \( A_g \): the surface area of gypsum; \( V \): the liquid volume in contact with the gypsum surface; \( IAP \): the product of ion activity; \( K \): ion solubility product. 

\( \frac{IAP}{K_{Gypsum}} \) is affected by the temperature; thus, it is the same as \( R_{Gypsum} \).
The solubility of gypsum in water reaches a maximum of 0.2097 g/100 g at 40 °C. The solubility decreases when the temperature is below or above 40 °C, the content of SO$_4^{2-}$ and Ca$^{2+}$ obtained by physical dissolution is very low.

3.2.2. Gypsum (CaSO$_4$) dissolved by glauber salt brine (Na$_2$SO$_4$)

Equations (2) and (3) show the reactions of Na$_2$SO$_4$ and CaSO$_4$ with water.

\[ \text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-} \quad (2) \]

\[ \text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} \quad (3) \]

Due to the common-ion effect, the solubility of the electrolyte will decrease when a strong electrolyte with the same ion is put into an electrolyte-saturated solution. Thus, the solubility of gypsum will be reduced when glauber salt brine flows through and dissolves the gypsum deposits, the gypsum will even harder to be dissolved in this situation. So if glauber salt brine flows through the gypsum deposits, the brine characteristic would not be changed apparently.

3.2.3. The reaction of trona brine or a mixture of trona and glauber salt brine with gypsum

The HCO$_3^-$ and CO$_3^{2-}$ contents in mixed brine or trona brine are very high and so are the solution alkalinity and pH. If the reaction kinetics is not taking into account, the pH has little influence on the dissolution of gypsum (Yang, 2003; Xu and Li, 2011). The reaction occurs when the brine with high concentrations of HCO$_3^-$ and CO$_3^{2-}$ flows through the gypsum deposits. The main chemical reactions are:
In Eq. (4), CaSO₄ is slightly soluble, while CaCO₃ is insoluble. The reaction easily occurs when insoluble substance is produced by slight soluble substance, the ionic equation is:

\[
\text{CO}_3^{2-} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}
\]  

(6)

The Gibbs Free Energy (\(\Delta G\)) is -22.7 kJ/mol under the standard state. When \(\Delta G\) is negative, the reaction, which is endothermic, happens freely. The reaction is faster at higher temperatures. Eq. (5) shows that \(\Delta G\) is 2102 kJ/mol under the standard state. When \(\Delta G\) is positive, the reaction will not happen freely.

Thus, the reaction shown in Eq. (5) won’t occur, the chemical reaction will still proceed as shown in Eq. (4), when trona brine or mixed brine flow through gypsum deposits.

### 3.2.4. The carbonate equilibrium effect during the reaction of different brine

The carbonate equilibrium that exists in trona brine or mixed brine is affected by pH. The carbonate in groundwater exists in three forms: free carbonic acid, bicarbonate and carbonic acid.

In trona brine (pH>10), concentration of HCO₃⁻ is 5-20 times the concentration of CO₃²⁻, and CO₃²⁻ in the brine is dominant in this case. When trona brine flows through the gypsum, CaSO₄ reacts with CO₃²⁻ and CaCO₃ precipitation is generated. If the concentration of CO₃²⁻ in brine decreases, the reversible reaction will take place and drive the equilibrium to the right. Thus, the reverse reaction
will occur when trona brine flows through the gypsum.  

\[ \text{CO}_3^{2-} + \text{CaSO}_4 \rightleftharpoons \text{SO}_4^{2-} + \text{CaCO}_3 \downarrow \]  

(7)  

\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]  

(8)  

The circular reactions as shown in Eqs. (7) and (8) will occur when mixed brine flows through the gypsum because of the similar properties with trona brine. Thus, taking the carbonate equilibrium effect into account, the concentration of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) will decrease, while \( \text{SO}_4^{2-} \) increases after CaCO\(_3\) precipitation was generated.  

3.3. Simulation of groundwater inrush source  

For further quantitative analysis of inrush water source and component, the international hydrological and geochemical simulation software PHREEQC was adopted to simulate the water-rock interaction. PHREEQC (DzavidL. Parkurst and C.A.J. Appelo, 1999) was exploited by USGS, it can calculate the geochemical action under temperature range of 0~300 degrees (Wei, 2010).  

Based on the deduction that the main water inrush source around Anpeng town was trona leakage brine, the research used the simulation method PHREEQC combined with the possible channel of inrush water to establish a conceptual model and then carried out hydrogeochemical simulation of the water-rock interaction. Subsequently, the research quantified the mixed ratio of inrush groundwater and shallow groundwater around Anpeng town, which can better verify the source of inrush water.
3.3.1. Conceptual model

Around Anpeng town, the trona leakage brine flowed through the specified mineral assemblages and mixed with shallow groundwater in different proportions.

3.3.2. Initial data input

The parameters of trona brine were taken from enterprise’s production testing data; the parameters of shallow groundwater were taken from the same aquifer but outside the study area, which can basically represent the groundwater background values. The specific parameters are shown in Table 1:

3.3.3. Setting of stratum and mineral

The formations from the bottom to top during the process of the leakage brine flowing into the shallow groundwater and then pouring out of the ground were as follows: third member of the Hetaoyuan Formation of Paleogene, Liaozhuang Formation, Fenghuang Formation of Neogene and Quaternary. To simplify the mining area, according to the thickness of rock stratum and the proportion of mineral composition, it can be assumed that the layer through which the trona brine flowed contains Ca-montmorillonite, kaolinite, gypsum, potash feldspar and potash mica.

The main ingredients are as follow: Kaolinite: \( \text{Al}_4[\text{Si}_2\text{O}_{10}]\text{(OH)}_8 \); Gypsum: \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \); Ca-montmorillonite: \( (\text{Na,Ca})_{0.33}(\text{Al, Mg})_2[\text{Si}_4\text{O}_{10}]\text{(OH)}_2\cdot n\text{H}_2\text{O} \); Dolomite: \( \text{CaCO}_3 \); Potash feldspar: \( \text{K}[\text{AlSi}_3\text{O}_8] \); Poash mica: aluminum silicate as K, Al, Mg, Fe and Li.
4. Results and Discussion

On 9 March, 2013, in Anpeng town, water samples from five groundwater inrush points and surrounding six water quality monitoring points (resident well) were tested, the result of water chemical composition are shown in Table 2, the distribution of sampling points is shown in Fig. 3.

According to the water quality analysis, the inrush brine had relatively high salinity, with some inrush water samples containing SO₄²⁻Na and some containing HCO₃⁻Na. The crystals mainly consist of Na₂SO₄, Na₂CO₃, and NaHCO₃. The composition of inrush water and the crystals were the same as those of the high-concentrated ions in the trona brine (Na₂CO₃, NaHCO₃, etc.) and glauber salt brine (Na₂SO₄).

4.1. The source of inrush water

The automatic water quality recorder was set up at the Y5 inrush point on 4 March, 2013. The monitoring time lasted from 5 March to 20 March, 2013. Thus, the relationship between the inrush points and the S02 well can be judged according to the correlation of the changes between temperature/electrical conductivity and the concentration of brine during the S02 production well reparation period (5-14 March, 2013).

The production of glauber was stopped during the investigation (March 2-15, 2013), so it could be judged how serious glauber mining affects water inrush hazard based on the dynamic water quality situation.
4.1.1. The source of inrush water in Y-5 point

After the successful reparation of the S02 well, the conductivity and temperature of inrush water decreased significantly. The CO$_3^{2-}$ concentration remained at 0, the concentration of HCO$_3^-$ decreased to 500meq/L, while the concentration of SO$_4^{2-}$ increased to 600meq/L. Subsequently, the concentrations of these three ions were in a state of dynamic balance. The analysis shows that the source of inrush water in Y-5 point is closely related to the S02 trona well.

In order to ensure that whether the glauber brine exists in this point as part of inrush source, further analysis had been performed. The depth of the well rupture was 234 m; gypsum deposit was developed in this depth. While the leakage of trona brine flowed through the gypsum deposit, reactions would happen as shown in Eqs. (7) and (8).

According to the ion milliequivalent concentrations (Ca$^{2+}$ 0.61meq/L; CO$_3^{2-}$ 905.3meq/L; HCO$_3^-$ 1332.94meq/L; Cl$^{-}$ 107.43meq/L; SO$_4^{2-}$ 267.89meq/L) of Y-5 point: the concentration of Ca$^{2+}$ was negligible compared with other main ions. Only the reaction between CO$_3^{2-}$ and CaSO$_4$ had to be taken into account because of the large number of CO$_3^{2-}$, fast flow speed, short contact time with gypsum and high temperature. The reaction of CO$_3^{2-}$ and CaSO$_4$ would take place at a ratio of 1:1 according to Eq. (7), and three types of inrush water sources could be assumed under this precondition:

1. Inrush water source only came from trona brine
The CO$_3^{2-}$ and CaSO$_4$ in the brine reacted at a ratio of 1:1, and the concentration of SO$_4^{2-}$ was equal to the reacted $\gamma$CO$_3^{2-}$ content. Thus, the $\gamma$CO$_3^{2-}$/$\gamma$HCO$_3^-$ ratio in the trona brine was equal to the $\gamma$(CO$_3^{2-}$+SO$_4^{2-}$)/$\gamma$HCO$_3^-$ ratio in the inrush water. From this calculation, it could be seen that $\gamma$(CO$_3^{2-}$+SO$_4^{2-}$)/$\gamma$HCO$_3^-$ was equal to 0.88, while $\gamma$CO$_3^{2-}$/$\gamma$HCO$_3^-$ ranged between 0.86 and 1.26. The content of $\gamma$(CO$_3^{2-}$+SO$_4^{2-}$)/$\gamma$HCO$_3^-$ was similar to $\gamma$CO$_3^{2-}$/$\gamma$HCO$_3^-$, therefore, the source of inrush water was exclusively trona brine.

(2) Inrush water source only came from glauber brine

The $\gamma$SO$_4^{2-}$/$\gamma$HCO$_3^-$ ratio in glauber brine was equal to 1237.8, while it was equal to 0.19 in inrush water. Therefore, the assumption was incorrect because of the widely varying ratio.

(3) Inrush water source came from the mixed brine of glauber and trona

Assuming that the contribution ratio of the glauber brine was x and that of the trona brine was y. If the assumption was true: 1237.8 × x + (0.86~1.26) × y = 0.88. This equation showed that when the contribution ratio of the trona brine was equal to 1, the contribution ratio of the glauber brine was equal to 1.6×10$^{-5}$, which was too small to ignore.

Thus, it could be confirmed that the water inrush source of Y-5 exclusively was the leakage trona brine coming from the broken S02 well.

4.1.2. The sources of inrush water in Y-4, Y-3, Y-2, Y-1 points

The inrush water quantity and dynamic variation of the concentration of SO$_4^{2-}$ and HCO$_3^-$ at
Y1-Y4 points were not obvious when the S02 well was under repair and all glauber wells were shut down (2-15 March). This result shows that the sources of these water inrush points were not due to the underground mining activities of glauber brine or the rupture of the S02 well, but because of the brine leakage coming from other trona wells.

### 4.1.3. Component and mixed proportion of inrush water

The PHREEQC simulation conditions were assumed as follow: (1) the trona brine did not mix with shallow groundwater after flowing through the mineral layer; (2) the trona brine mixed with shallow groundwater under the ratio of 1:2, 1:10, 1:100, 1:200, 1:500, 1:1000 and 1:5000 after flowing through the mineral layer. The simulation results are shown in Table 3.

Table 3 shows that when the trona brine flowed through the stratum and shallow groundwater, the concentrations of Na⁺, Cl⁻ and SO₄²⁻ decreased while the concentration of HCO₃⁻ increased with the increasing proportion of the shallow water. The concentration of Ca²⁺ decreased at first and then increases.

The ion concentrations in Y-5, except for SO₄²⁻, were similar to the ion concentrations in trona brine. However, at the same time, the concentration of HCO₃⁻ was almost 0. When the trona brine flowed through the layer, it would react rapidly and pour out of the ground directly because of the fast speed of inrush water in Y-5. Meanwhile, the trona brine was not continuously provided in the simulation. Thus, the concentration of HCO₃⁻ would be close to the concentration of trona brine in
reality. Therefore, the trona brine must be a great deal of rapid inrush, nearly not mixing with shallow groundwater.

The PHREEQC simulation analysis result shows that: the water inrush source of Y-5 was nearly all of the trona brine from the ruptured SO2 well; the water inrush source of Y-3 was a mixture of trona brine and groundwater under the ratio of 1:10~1:100, while the water inrush sources of Y-4, Y-2 and Y-1 were a mixture of trona brine and groundwater under the ratio of 1:200.

4.2. The channel of inrush water

4.2.1. Reason for brine leakage

Trona is produced by either single well or double/multiple well convection mining method, which belongs to water soluble mining method (Lin, 1987). The main mining unit is consisting of salt cavity and production well. Thus, the instability of salt cavity and the rupture of production well are the main possible reasons for brine leakage.

(1) Analysis of the salt cavity stability

The possibility of salt cavity collapse: Trona mineral is distributed at the bottom of the second member of the Hetaoyuan Formation and in the upper part of the third member of the Hetaoyuan Formation, with dolomite strata developed in the roof and floor. The thick and hard surrounding rock structure determines that the cavity produced by hydrofracture is hard to fill with large-scale fractured channels and can remain intact and stable.
The development of roof fracture: When a mineral is under exploiting, the surrounding rock in the cavity is under the pressure from the inner brine. This pressure is equal to the water injection pressure plus the water column pressure in the production well. The water injection pressure of trona production well is approximately 10-20 MPa, meanwhile the 1560.92-2929.53 m (mineral buried depth) water column pressure is approximately 15.3-28.71 MPa. Thus, the biggest water pressure on the surrounding rock in the cavity is 48.71 MPa. The main lithology of the surrounding rock is dolomite which is 500 m in thickness and 142.66 MPa in compressive strength, this compressive strength is 3 times that of the biggest water pressure. Therefore, large-scale fractures in the surrounding rock of trona mineral is difficult to develop under the effect of sustain water pressure.

(2) Analysis of production well rupture

The phenomenon of brine leakage caused by S02 well rupture in Anpeng town indicates that production well damage is an important reason for brine leakage. The depth of the S02 well rupture is 234 m underground, i.e., in the gypsum deposit, which is strongly hygroscopic. The pressure caused by water swelling is approximately 0.15 MPa (Li and Zhou, 1996), which may damage the production well and induce brine leakage. The high concentration of SO\textsubscript{4}\textsuperscript{2-} (>250 mg/L) generated by reaction of leakage brine and gypsum can also corrode the production well and lead to groundwater inrush.

4.2.2. Analysis of water-conducting channel

According to our analysis, the most probable reason for brine leakage in trona is the production...
well rupture. The leaking brine will flow along the water-conducting channel into the shallow aquifer and even pour out to the ground. However the geological structure in the mining area shows no water-conducting fault development. Thus, the water-conducting channel, which the leakage brine flows along, is probably fissure or artificial channel.

Structural fissure is the main type of fissure that appears in groundwater inrush hazard when using solution mining method. The structural fissure is determined by maximum horizontal principal stress, which is controlled by the tectonic stress field in the mining area. The connection direction of the S02 well and other water inrush points is NW-SE, which is the same as that of the structural fissure zone development direction. This indicates that the main water-conducting channel in Anpeng town is controlled by the structural fissure zone.

The inrush points in Anpeng town are all located at the abandoned gypsum exploitation wells, which were not strictly closed. Thus, the high-pressure cavity water or leakage brine can flow along the structural fissure zone; finally connect with these wells, and then pour out of the ground through boreholes. Therefore, the abandoned gypsum exploitation wells are the main channels through which shallow polluted groundwater gushed out of the ground, as shown in Fig. 4.

5. Conclusions

This study aimed at investigating the source and channel of inrush water in a multilayer rock salt mine area. To achieve the set objectives, this study combined analysis of geological and
hydrogeological conditions, analysis of physical and chemical reaction principle of different brines, PHREEQC simulation method, and analysis of geological and artificial reason on the conducting channel where leakage brine flowed from the damage depth to the ground as the study methodology.

Long-term solution mining with high-pressure and -temperature water not only dissolves minerals but also may cause rupture of strata and damage of production well, which usually results in brine leakage or the inrush of groundwater. Geological and hydrogeological conditions are the basis which determines the total risk of groundwater inrush hazard. Physical and chemical reaction principle analysis of different brines and hydrogeochemical simulation of water-rock interaction in different assumed conditions by PHREEQC simulation method can not only determine the exact source of leakage brine but also identify the mixed proportion of inrush water while the leakage brine flows through the mineral layer in different way. Besides geological reason, mining technic such as pressure control of injection water, groundwater quality monitoring of exploitation wells may also determines the risk of a groundwater inrush hazard in a multilayer rock salt mine area.

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Author Contributions

Bin Zeng and Tingting Shi contributed to data analysis and manuscript writing; Zhihua Chen
proposed the main structure of this study; Liu Xiang and Muyi Yang designed and performed the experiments; Shaopeng Xiang performed the PHREEQC simulation. All authors read and approved the final manuscript.

**Conflicts of Interest**

The authors declare that they have no conflict of interest.
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Figure captions

**Fig. 1.** One of the long-term (more than 2 years) groundwater inrush points with stable discharge (Y-3).

**Fig. 2.** The sudden groundwater inrush point (Y-5). As shown in this figure, the high-temperature inrush groundwater was being pumped after the ground was broken.

**Fig. 3.** Information about strata, lithology, aquifer, and buried position of each ore bed in the mining area.

**Fig. 4.** Sketch map of hydrogeological conditions and distribution of groundwater inrush points in mining area.

**Fig. 5.** Schematic diagram of source and channel analysis of groundwater inrush hazard in the multilayer rock salt mine area in Tongbai County.
<table>
<thead>
<tr>
<th>System</th>
<th>Series</th>
<th>Formation</th>
<th>Member</th>
<th>Thickness (m)</th>
<th>Lithologic profile</th>
<th>Petrographic description</th>
<th>Minerals</th>
<th>Aquifer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Neogean</td>
<td>Oligocene</td>
<td>Mankuang shales</td>
<td></td>
<td>6-280</td>
<td></td>
<td>Alternating layers of glutenite and sandy clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Upper part: mudstone is interbedded with gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lower part: Alternating layers of mudstone and glutenite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palaeogene</td>
<td>Eocene</td>
<td>Henan</td>
<td>Second segment</td>
<td>400-500</td>
<td>Mudstone with interlayers of glutenite, as well as thin layers of shale, muddy dolomite and glauconite’s salt</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>First segment</td>
<td>700-800</td>
<td>Mudstone is interlayered with muddy dolomite and dolomite, as well as small amounts of trona</td>
<td></td>
<td></td>
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</tbody>
</table>

**Legend**

- Glutenite
- Sandy clay
- Mudstone
- Muddy dolomite
- Shale
- Siltstone
- Dolomite
- Mineral vein

Fig. 3
Fig. 4
Fig. 5
Table 1 Initial data of trona brine and background value of groundwater for PHREEQC simulation

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
<th>CO₃²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trona brine</td>
<td>70.0</td>
<td>10.8</td>
<td>85880</td>
<td>5.0</td>
<td>1.0</td>
<td>3819</td>
<td>206.0</td>
<td>104721</td>
<td>4565</td>
</tr>
<tr>
<td>Background value of groundwater</td>
<td>14.1</td>
<td>7.5</td>
<td>38.76</td>
<td>67.10</td>
<td>23.88</td>
<td>12.46</td>
<td>39.31</td>
<td>386.87</td>
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Table 2 Chemical composition of groundwater from inrush hazard points and surrounding resident wells

<table>
<thead>
<tr>
<th>Source Point</th>
<th>Na$^+$ (mg/L)</th>
<th>Ca$^{2+}$ (mg/L)</th>
<th>Mg$^{2+}$ (mg/L)</th>
<th>Cl$^-$ (mg/L)</th>
<th>SO$_4^{2-}$ (mg/L)</th>
<th>HCO$_3^-$ (mg/L)</th>
<th>CO$_3^{2-}$ (mg/L)</th>
<th>Salinity (mg/L)</th>
<th>Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater from inrush hazard points</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y-1</td>
<td>447.30</td>
<td>91.2</td>
<td>74.68</td>
<td>171.18</td>
<td>278.55</td>
<td>1488.89</td>
<td>0.00</td>
<td>1807.35</td>
<td></td>
</tr>
<tr>
<td>Y-2</td>
<td>524.50</td>
<td>89.34</td>
<td>75.32</td>
<td>153.97</td>
<td>298.88</td>
<td>1525.00</td>
<td>0.00</td>
<td>1904.51</td>
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<tr>
<td>Y-3</td>
<td>1132.00</td>
<td>146.6</td>
<td>158.30</td>
<td>125.56</td>
<td>4296.44</td>
<td>1012.93</td>
<td>0.00</td>
<td>6365.37</td>
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<tr>
<td>Y-4</td>
<td>50300.00</td>
<td>12.23</td>
<td>53.21</td>
<td>12858.63</td>
<td>81309.15</td>
<td>27159.0</td>
<td>107692.4</td>
<td></td>
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<tr>
<td>Groundwater from resident wells around the inrush points</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SY-1</td>
<td>46.28</td>
<td>76.76</td>
<td>17.29</td>
<td>64.3</td>
<td>14.58</td>
<td>319.03</td>
<td>0.00</td>
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<tr>
<td>SY-2</td>
<td>28.37</td>
<td>98.02</td>
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<td>10.38</td>
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<tr>
<td>SY-3</td>
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<td>0.00</td>
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<tr>
<td>SY-5</td>
<td>31.67</td>
<td>95.51</td>
<td>19.22</td>
<td>53.93</td>
<td>22.59</td>
<td>351.97</td>
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<td>398.9</td>
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<tr>
<td>SY-6</td>
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<td>68.82</td>
<td>19.6</td>
<td>18.51</td>
<td>21.55</td>
<td>340.38</td>
<td>0.00</td>
<td>335.43</td>
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</table>
Table 3 Simulation results for mixed proportion of inrush trona brine by PHREEQC (mg/L)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Mixed proportion with shallow groundwater</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
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<tr>
<td>Unmixing</td>
<td>87147.00</td>
<td>301.08</td>
<td>3880.15</td>
<td>68659.20</td>
<td>5.06</td>
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<tr>
<td>Trona brine unmixed or mixed with different proportion of shallow groundwater after flowing through the mineral layer (simulation results)</td>
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<tr>
<td>1:1</td>
<td>48093.00</td>
<td>280.00</td>
<td>2145.62</td>
<td>37900.80</td>
<td>9.39</td>
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<tr>
<td>1:2</td>
<td>33235.00</td>
<td>184.72</td>
<td>1485.68</td>
<td>26188.80</td>
<td>13.97</td>
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<tr>
<td>1:10</td>
<td>9586.40</td>
<td>148.28</td>
<td>436.30</td>
<td>7561.92</td>
<td>57.95</td>
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<tr>
<td>1:100</td>
<td>1098.25</td>
<td>90.40</td>
<td>141.63</td>
<td>873.89</td>
<td>306.34</td>
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<tr>
<td>1:200</td>
<td>571.78</td>
<td>69.60</td>
<td>118.56</td>
<td>459.17</td>
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<td>1:500</td>
<td>252.77</td>
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<td>104.60</td>
<td>207.84</td>
<td>453.66</td>
<td></td>
</tr>
<tr>
<td>1:1000</td>
<td>144.81</td>
<td>67.52</td>
<td>99.94</td>
<td>105.12</td>
<td>481.60</td>
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<td>Water quality test results in five water inrush hazard points</td>
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<tr>
<td>Y-1</td>
<td>447.30</td>
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<td>81309.15</td>
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</tr>
</tbody>
</table>

Table 3 Simulation results for mixed proportion of inrush trona brine by PHREEQC (mg/L)