



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

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5 Bin Zeng^{1*}, Tingting Shi², Zhihua Chen¹, Liu Xiang³, Shaopeng Xiang⁴, Muye Yang¹

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7 ¹. School of Environmental Studies, China University of Geosciences, Wuhan 430074, Hubei, P.R.China.

8 ². Three Gorges Research Center for Geo-Hazard, Ministry of Education, Wuhan 430074, Hubei, P.R.China.

9 ³. Department of Geological Engineering, Hubei Land Resources Vocational College. Wuhan 430074, P.R.China.

10 ⁴. Hydrological Engineering Environment Technology Consulting Co. Ltd. Wuhan 430074, P.R.China.

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12 ***Corresponding author:** Bin Zeng, Ph.D.

13 Affiliation: School of Environmental Studies, China University of Geosciences.

14 Affiliation address: No. 388 Lumo Road, Wuhan, Hubei, 430074, P.R. China.

15 Email: zengbin_19@126.com. Tel: 86-27-67883473. Fax: 86-27-87436235.

16



17 **ABSTRACT**

18 The solution mining of salt mineral resources may contaminate groundwater and lead to water
19 intrush out of the ground due to brine leakage. Taking a serious groundwater intrush hazard in a large
20 salt mining area with three different types of ore beds which are trona (trisodium hydrogencarbonate
21 dihydrate, also sodium sesquicarbonate dihydrate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, is a non-marine evaporite
22 mineral), glauber (sodium sulfate, is the inorganic compound with formula Na_2SO_4 as well as several
23 related hydrates) and gypsum (a soft sulfate mineral composed of calcium sulfate dihydrate, with
24 the chemical formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in Tongbai County of China as an example, this paper mainly
25 aims to analyse the source and channel of the intrush water. Based on the understanding of geological
26 and hydrogeological conditions, the study obtained hydrochemical data of groundwater at different
27 points and depths first; and then analysed the pollution source and pollutant component from single or
28 mixed brines by both physical-chemical reaction principle analysis and hydrogeochemistry simulation
29 method; finally possible leakage brine conducting channel to the ground had been discussed from both
30 geological and artificial aspects. The results reveal that the brine from the trona mine is the major
31 pollution source; the fissure zone in NW-SE direction controlled by the geological structure provides
32 the main channels for the leakage brine to flow into the aquifer around the water intrush regions, and a
33 large number of waste gypsum exploration boreholes are the channels that supply the polluted
34 groundwater intrush out of the ground. The research can offer a valuable reference for avoiding and
35 assessing groundwater intrush hazard in similar rock salt mining area, which is advantageous for both
36 groundwater quality protection and resident health.



37 **1. Introduction**

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

46 Many scholars (Clark and Fritz, 1997; Liu et al., 2015; Wu et al., 2016) have studied the case of
47 groundwater inrush hazards in both coal and metal mines, and some adopted methods are as follow:
48 the use of water level/temperature criterion (Yuan and Gui, 2005; Ma and Qian, 2014), stochastic
49 simulation (Fernandez-Galvez et al., 2007), numerical simulation (Liu et al., 2009; Kang et al., 2012;
50 Shao et al., 2013; Houben, et al., 2017), water chemical analysis (Robins, 2002; Fernandez et al., 2005;
51 Hu et al., 2010; Cobbina et al., 2015; Lee et al., 2016; LeDoux et al., 2016) (isotope analysis, water
52 quality type correlation analysis), multivariate statistics (Chen and Li, 2009; Lu, 2012) (discriminant
53 analysis, clustering analysis) , fractional advection dispersion equations (Ramadas et al., 2015) and
54 nonlinear analysis (Hao et al., 2010; Gao, 2012) (fuzzy mathematics, grey correlation analysis, etc.).



55 However, due to the particularity of mining method (solution mining) and complex chemical-physical
56 reactions during mining process (under high-pressure and -temperature), research about solution
57 mining is more focusing on mining techniques (Jiang and Jiang, 2004; Kotwica, 2008; Namin et al.,
58 2009), mining cavity stability analysis and sinkhole problem (Staudtmeister and Rokahr, 1997;
59 Bonetto et al., 2008; Ezersky et al., 2009; Goldscheider and Bechtel, 2009; Closson and Abou Karaki,
60 2009; Vigna et al., 2010; Frumkin et al., 2011; Ezersky and Frumkin, 2013; Qiu, 2011; Blachowski et
61 al., 2014), and geohazards especially in karst area due to human-induced underground caves (Waltham
62 and Fookes 2003; Parise and Gunn 2007; Zhou and Beck 2011; Parise and Lollino 2011; Lollino et al.,
63 2013; Gutierrez et al., 2014; Parise et al., 2015), but rarely on the source and channel analysis of
64 inrush water in solution mining accident.

65 The studied rock salt mine area is located in Tongbai County of Henan province in China. This
66 mine area has the second largest trona reserves worldwide, while its glauber salt reserves reaches 45
67 million tons. Since trona and glauber salt had been put into production in 1990 with single and double
68 well convection mining as their main producing method, from June 2011 to May 2013, five inrush
69 points appeared in Anpeng Town of Tongbai County. Among these five inrush points, four (Y1~Y4)
70 were long-term (more than 2 years) inrush points with stable discharge, while one (Y-5) was a sudden
71 inrush point (as shown in Fig. 1 and Fig. 3). On 1 February, 2013, almost 200 m³ of mud and sediment
72 erupted out of the ground at Y-5 point. The area of inrush point was almost 4 m²; the average water



73 inflow was 20-30 m³/d while the largest inflow reached 200m³/d, and the water inrush lasted for
74 approximately 3 months. During the Y-5 inrush accident, according to the field investigation, a trona
75 production well named “S02”, which is 200 m away from the inrush point, was broken at the depth of
76 234 m for a long period of time, and it was repaired on 15 March, 2013. During the whole water inrush
77 process, the inrush groundwater led to the phenomenon of salinization at the house bottom in many
78 villagers, and made water in many resident wells undrinkable any more.

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

86 **2. Geological and hydrogeological setting**

87 ***2.1. Geological conditions***

88 The mining area is located in northwest of Tongbai County. The landscape is characterized by
89 hollows and ridges, and has an elevation ranging between 140 and 200 m. Information about the strata,
90 lithology, aquifer, and position of different ore beds in research area (Shi et al., 2013) are shown in Fig.



91 2.

92 According to the field investigation, in the mining area, some buried faults develop in the
93 Hetaoyuan Formation, but these faults have only small effect on the ore bed because they are either
94 outside of the ore bed or distribute in a limited area.

95 **2.2. Hydrogeological conditions**

96 The groundwater in the mining area can be divided into pore water in the loose rock mass and
97 bedrock fissure water according to lithology and hydrogeological features. In the upper part of
98 Liaozhuang Formation, mudstone interbedded with gypsum is considered as the aquiclude. The
99 shallow aquifer is an unconsolidated pore water aquifer located above the aquiclude, while the deep
100 aquifer is a bedrock fissure aquifer located under the aquiclude. The water inflow of a single well with
101 poor water content is approximately 100m³/d, while it can reach 1000-2000 m³/d with rich water
102 content. The annual variation of groundwater level is 2-4 m, while the depth is stable at 2.3-4 m.
103 Residents in Anpeng Town take groundwater as source of drinking water, which comes from the well
104 and belongs to porous aquifer.

105 As shown in Fig. 2, gypsum mainly exists on the top of the Liaozhuang Formation, glauber salt
106 exists in the third member of the Hetaoyuan Formation, and trona exists at the bottom of the second
107 member of the Hetaoyuan Formation and on top of the first member of the Hetaoyuan Formation. The
108 surrounding rocks of every mineral layer include mudstone, shale, psammitic rock and dolomite,



109 which have sufficient thickness and good water-resistance ability. Therefore, the effect of groundwater
110 on the mineral deposit is minimal in the mining area.

111 ***2.3 Distribution and characteristics of the ore body***

112 The three ore bodies overlap in plane distribution, as shown in Fig. 3. The vertical distribution of
113 ore bodies from deep to shallow is trona (buried depth: 1560.92-2929.53 m), glauber salt (buried
114 depth: 1003.66-1397.58m) and gypsum (buried depth: 134-338 m). Trona and glauber salt are at least
115 250 m apart from each other vertically.

116 Trona has 11 horizontal layers, with an average thickness of 2.11m. The chemical composition of
117 trona is mainly NaHCO_3 (average of 77.06%) and Na_2CO_3 (average of 16.33%) (Wang, 1987).
118 Glauber salt has 4 layers, with an average thickness of 8.93m. The dip angle of ore bed layer is within
119 10° . The average mineral grade is 60.14%. The main composition of glauber salt is Na_2SO_4 (>90%),
120 and with a small amount of NaCl.

121 **3. Methods**

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

125 ***3.1. Sampling and test***

126 The 5 groundwater inrush points (Y1~Y5) and some shallow groundwater points (resident wells):



127 SY1~SY6) nearby the accident site were chosen as groundwater quality sampling points, as shown in
128 Fig. 3. Water from each point was sampled on 9 March, 2013.

129 Water samples were filtered by 0.45 μm millipore filtration membrane in the field, and then filled
130 with a polyethylene bottle which had been soaked in acid and washed with de ionized water. Filtered
131 water samples were acidized until $\text{pH}<2$ by addition of ultra-pure HNO_3^- for the determination of
132 cation; water samples for the determination of anion would not be treated.

133 Elements tested in laboratory include 26 cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , etc.) and 5 anions (F^- ,
134 Cl^- , NO_3^- , SO_4^{2-} , NO_2^-). The instrument for the determination of cation is inductively coupled plasma
135 atomic emission spectrometer (Agilent ICP-OES 5100), while the minimum detection limit is
136 0.0001mg/L; the instrument for the determination of anion is ion chromatograph (ICS-1100), while
137 the minimum detection limit is 0.001 mg/L. CO_3^{2-} and HCO_3^- were tested according to “Groundwater
138 quality test method: Determination of carbonate and bicarbonate by hydroxide titration (DZ/T
139 0064.49-93)”, while the minimum detection limit is 0.01 mg/L.

140 In addition, from March to April 2013, at Y-5 and Y-3 points, three water quality automatic
141 recorders (Levellogger gold, Canada) were arranged for the inrush water monitoring. Monitoring
142 indicators were temperature, water level and electrical conductivity. The monitoring purpose was to
143 master the inrush water quality during the whole accident, especially in the process of well repairation.



144 **3.2. Analysis on physical and chemical reaction principle in different brine mixing conditions**

145 During the accident, the leakage brine of trona (2000 m below the ground) or glauber salt mine
146 (1000 m below the ground) might flow through the gypsum deposit (200-400 m below the ground,
147 comprising primarily CaSO_4) and caused physical and chemical reactions while inrush out of the
148 ground. So the formation of inrush water chemistry component might be by glauber brine, or trona brine,
149 or a mixture of the two brines flowed through the gypsum layer with physical and chemical reaction. To
150 provide the basis for further analysis of the inrush water source, the physical solubility of gypsum, the
151 reaction when glauber salt brine, trona brine, mixture of trona and glauber salt brine flow through the
152 gypsum deposits were analysed.

153 **3.2.1. The physical solubility of gypsum (CaSO_4)**

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

156
$$R_{\text{Gypsum}} = k_1 \times \frac{A_g}{V} \left(1 - \left(\frac{\text{IAP}}{K}\right)_{\text{Gypsum}}\right) \quad (1)$$

157 R_{Gypsum} : the dissolution rate of gypsum; k_1 : rate constant; A_g : the surface area of gypsum; V : the
158 liquid volume in contact with the gypsum surface; IAP : the product of ion activity; K : ion solubility
159 product.

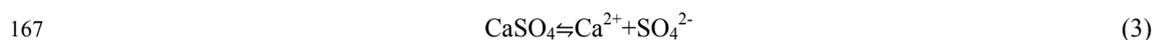
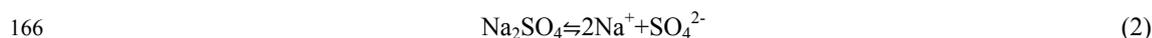
160 $\left(\frac{\text{IAP}}{K}\right)_{\text{Gypsum}}$ is affected by the temperature; thus, it is the same as R_{Gypsum} .



161 The solubility of gypsum in water reaches a maximum of 0.2097 g/100 g at 40°C. The solubility
162 decreases when the temperature is below or above 40°C, the content of SO_4^{2-} and Ca^{2+} obtained by
163 physical dissolution is very low.

164 3.2.2. Gypsum (CaSO_4) dissolved by glauber salt brine (Na_2SO_4)

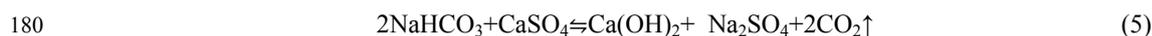
165 Equations (2) and (3) show the reactions of Na_2SO_4 and CaSO_4 with water.



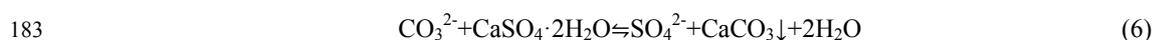
168 Due to the common-ion effect, the solubility of the electrolyte will decrease when a strong
169 electrolyte with the same ion is put into an electrolyte-saturated solution. Thus, the solubility of gypsum
170 will be reduced when glauber salt brine flows through and dissolves the gypsum deposits,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

173 3.2.3. The reaction of trona brine or a mixture of trona and glauber salt brine with gypsum

174 The HCO_3^- and CO_3^{2-} contents in mixed brine or trona brine are very high and so are the solution
175 alkalinity and pH. If the reaction kinetics is not taking into account, the pH has little influence on the
176 dissolution of gypsum (Yang, 2003; Xu and Li, 2011). The reaction occurs when the brine with high
177 concentrations of HCO_3^- and CO_3^{2-} flows through the gypsum deposits. The main chemical reactions
178 are:



181 In Eq. (4), CaSO_4 is slightly soluble, while CaCO_3 is insoluble. The reaction easily occurs when
182 insoluble substance is produced by slight soluble substance, the ionic equation is:



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

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

190 3.2.4. The carbonate equilibrium effect during the reaction of different brine

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

193 In trona brine ($\text{pH} > 10$), concentration of HCO_3^- is 5-20 times the concentration of CO_3^{2-} , and
194 CO_3^{2-} in the brine is dominant in this case. When trona brine flows through the gypsum, CaSO_4 reacts
195 with CO_3^{2-} and CaCO_3 precipitation is generated. If the concentration of CO_3^{2-} in brine decreases, the
196 reversible reaction will take place and drive the equilibrium to the right. Thus, the reverse reaction



197 will occur when trona brine flows through the gypsum.



200 The circular reactions as shown in Eqs. (7) and (8) will occur when mixed brine flows through the
201 gypsum because of the similar properties with trona brine. Thus, taking the carbonate equilibrium
202 effect into account, the concentration of HCO_3^- and CO_3^{2-} will decrease, while SO_4^{2-} increases after
203 CaCO_3 precipitation was generated.

204 ***3.3. Simulation of groundwater inrush source***

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

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



214 3.3.1. *Conceptual model*

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

217 3.3.2. *Initial data input*

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

221 3.3.3. *Setting of stratum and mineral*

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

228 The main ingredients are as follow: Kaolinite: $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$; Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$;
229 Ca-montmorillonite: $(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2[\text{Si}_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$; Dolomite: CaCO_3 ; Potash feldspar: K
230 $[\text{AlSi}_3\text{O}_8]$; Poash mica: aluminum silicate as K, Al, Mg, Fe and Li.



231 **4. Results and Discussion**

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

235 According to the water quality analysis, the inrush brine had relatively high salinity, with some
236 inrush water samples containing SO_4Na and some containing HCO_3Na . The crystals mainly consist
237 of NaSO_4 , Na_2CO_3 , and NaHCO_3 . The composition of inrush water and the crystals were the same as
238 those of the high-concentrated ions in the trona brine (Na_2CO_3 , NaHCO_3 , etc.) and glauber salt brine
239 (Na_2SO_4).

240 **4.1. The source of inrush water**

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

246 The production of glauber was stopped during the investigation (March 2-15, 2013), so it could be
247 judged how serious glauber mining affects water inrush hazard based on the dynamic water quality
248 situation.



249 *4.1.1. The source of inrush water in Y-5 point*

250 After the successful reparation of the S02 well, the conductivity and temperature of inrush water
251 decreased significantly. The CO_3^{2-} concentration remained at 0, the concentration of HCO_3^- decreased
252 to 500meq/L, while the concentration of SO_4^{2-} increased to 600meq/L. Subsequently, the
253 concentrations of these three ions were in a state of dynamic balance. The analysis shows that the
254 source of inrush water in Y-5 point is closely related to the S02 trona well.

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

259 According to the ion milliequivalent concentrations (Ca^{2+} 0.61meq/L; CO_3^{2-} 905.3meq/L; HCO_3^-
260 1332.94meq/L; Cl^- 107.43meq/L; SO_4^{2-} 267.89meq/L) of Y-5 point: the concentration of Ca^{2+} was
261 negligible compared with other main ions. Only the reaction between CO_3^{2-} and CaSO_4 had to be
262 taken into account because of the large number of CO_3^{2-} , fast flow speed, short contact time with
263 gypsum and high temperature. The reaction of CO_3^{2-} and CaSO_4 would take place at a ratio of 1:1
264 according to Ep. (7), and three types of inrush water sources could be assumed under this
265 precondition:

266 (1) Inrush water source only came from trona brine



267 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
268 equal to the reacted γCO_3^{2-} content. Thus, the $\gamma\text{CO}_3^{2-}/\gamma\text{HCO}_3^-$ ratio in the trona brine was equal to the
269 $\gamma(\text{CO}_3^{2-}+\text{SO}_4^{2-})/\gamma\text{HCO}_3^-$ ratio in the inrush water. From this calculation, it could be seen that
270 $\gamma(\text{CO}_3^{2-}+\text{SO}_4^{2-})/\gamma\text{HCO}_3^-$ was equal to 0.88, while $\gamma\text{CO}_3^{2-}/\gamma\text{HCO}_3^-$ ranged between 0.86 and 1.26. The
271 content of $\gamma(\text{CO}_3^{2-}+\text{SO}_4^{2-})/\gamma\text{HCO}_3^-$ was similar to $\gamma\text{CO}_3^{2-}/\gamma\text{HCO}_3^-$, therefore, the source of inrush water
272 was exclusively trona brine.

273 (2) Inrush water source only came from glauber brine

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

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

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

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

283 *4.1.2. The sources of inrush water in Y-4, Y-3, Y-2, Y-1 points*

284 The inrush water quantity and dynamic variation of the concentration of SO_4^{2-} and HCO_3^- at



285 Y1-Y4 points were not obvious when the S02 well was under repair and all glauber wells were shut
286 down (2-15 March). This result shows that the sources of these water inrush points were not due to the
287 underground mining activities of glauber brine or the rupture of the S02 well, but because of the brine
288 leakage coming from other trona wells.

289 *4.1.3. Component and mixed proportion of inrush water*

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

294 Table 3 shows that when the trona brine flowed through the stratum and shallow groundwater, the
295 concentrations of Na^+ , Cl^- and SO_4^{2-} decreased while the concentration of HCO_3^- increased with the
296 increasing proportion of the shallow water. The concentration of Ca^{2+} decreased at first and then
297 increases.

298 The ion concentrations in Y-5, except for SO_4^{2-} , were similar to the ion concentrations in trona
299 brine. However, at the same time, the concentration of HCO_3^- was almost 0. When the trona brine
300 flowed through the layer, it would react rapidly and pour out of the ground directly because of the fast
301 speed of inrush water in Y-5. Meanwhile, the trona brine was not continuously provided in the
302 simulation. Thus, the concentration of HCO_3^- would be close to the concentration of trona brine in



303 reality. Therefore, the trona brine must be a great deal of rapid inrush, nearly not mixing with shallow
304 groundwater.

305 The PHREEQC simulation analysis result shows that: the water inrush source of Y-5 was nearly
306 all of the trona brine from the ruptured S02 well; the water inrush source of Y-3 was a mixture of trona
307 brine and groundwater under the ratio of 1:10~1:100, while the water inrush sources of Y-4, Y-2 and
308 Y-1 were a mixture of trona brine and groundwater under the ratio of 1:200.

309 ***4.2. The channel of inrush water***

310 *4.2.1. Reason for brine leakage*

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

315 (1) Analysis of the salt cavity stability

316 The possibility of salt cavity collapse: Trona mineral is distributed at the bottom of the second
317 member of the Hetaoyuan Formation and in the upper part of the third member of the Hetaoyuan
318 Formation, with dolomite strata developed in the roof and floor. The thick and hard surrounding rock
319 structure determines that the cavity produced by hydrofracture is hard to fill with large-scale fractured
320 channels and can remain intact and stable.



321 The development of roof fracture: When a mineral is under exploiting, the surrounding rock in the
322 cavity is under the pressure from the inner brine. This pressure is equal to the water injection pressure
323 plus the water column pressure in the production well. The water injection pressure of trona
324 production well is approximately 10-20 MPa, meanwhile the 1560.92-2929.53 m (mineral buried
325 depth) water column pressure is approximately 15.3-28.71 MPa. Thus, the biggest water pressure on
326 the surrounding rock in the cavity is 48.71 MPa. The main lithology of the surrounding rock is
327 dolomite which is 500 m in thickness and 142.66 MPa in compressive strength, this compressive
328 strength is 3 times that of the biggest water pressure. Therefore, large-scale fractures in the
329 surrounding rock of trona mineral is difficult to develop under the effect of sustain water pressure.

330 (2) Analysis of production well rupture

331 The phenomenon of brine leakage caused by S02 well rupture in Anpeng town indicates that
332 production well damage is an important reason for brine leakage. The depth of the S02 well rupture is
333 234 m underground, i.e., in the gypsum deposit, which is strongly hygroscopic. The pressure caused
334 by water swelling is approximately 0.15 MPa (Li and Zhou, 1996), which may damage the production
335 well and induce brine leakage. The high concentration of SO_4^{2-} (>250 mg/L) generated by reaction of
336 leakage brine and gypsum can also corrode the production well and lead to groundwater inrush.

337 4.2.2. Analysis of water-conducting channel

338 According to our analysis, the most probable reason for brine leakage in trona is the production



339 well rupture. The leaking brine will flow along the water-conducting channel into the shallow aquifer
340 and even pour out to the ground. However the geological structure in the mining area shows no
341 water-conducting fault development. Thus, the water-conducting channel, which the leakage brine
342 flows along, is probably fissure or artificial channel.

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

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

354 **5. Conclusions**

355 This study aimed at investigating the source and channel of inrush water in a multilayer rock salt
356 mine area. To achieve the set objectives, this study combined analysis of geological and



357 hydrogeological conditions, analysis of physical and chemical reaction principle of different brines,
358 PHREEQC simulation method, and analysis of geological and artificial reason on the conducting
359 channel where leakage brine flowed from the damage depth to the ground as the study methodology.

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

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373 **Author Contributions**

374 Bin Zeng and Tingting Shi contributed to data analysis and manuscript writing; Zhihua Chen



375 proposed the main structure of this study; Liu Xiang and Muye Yang designed and performed the
376 experiments; Shaopeng Xiang performed the PHREEQC simulation. All authors read and approved
377 the final manuscript.

378 **Conflicts of Interest**

379 The authors declare that they have no conflict of interest.

380



381 **References**

- 382 Bonetto, S., Fiorucci, A., Fornaro, M. and Vigna, B.: Subsidence hazards connected to quarrying
383 activities in a karst area: the case of the Moncalvo sinkhole event (Piedmont, NW Italy),
384 Estonian J. Earth Sci., 57, 125-134, 2008
- 385 Blachowski, J., Milczarek, W. and Stefaniak, P.: Deformation information system for facilitating
386 studies of mining-ground deformations, development, and applications, Nat. Hazards Earth
387 Syst. Sci., 14, 1677-1689, 2014
- 388 Clark, I. D. and Fritz, P.: Environmental isotopes in hydrogeology, Lewis Publishers, New York,
389 USA, 35-37, 1997.
- 390 Chen, H. J. and Li, X. Bi.: Studies of water source determination method of mine water inrush
391 based on Bayes' multi-group stepwise discriminant analysis theory, Rock and Soil
392 Mechanics., 30, 3655-3659, 2009.
- 393 Closson, D. and Abou Karaki, N.: Salt karst and tectonics: sinkholes development along tension
394 cracks between parallel strike-slip faults , Dead Sea , Jordan. Earth Surface Processes and
395 Landforms., 1408-1421, 2009
- 396 Cobbina, S.J., Duwiejuah, A.B., Quansah, R., Obiri, S. and Bakobie, Noel.: Comparative
397 Assessment of Heavy Metals in Drinking Water Sources in Two Small-Scale Mining
398 Communities in Northern Ghana, Int. J. Environ. Res. Public Health., 12, 10620-10634,



- 399 2015.
- 400 Ezersky, M., Legchenko, A., Camerlynck, C. and Al-Zoubi, A.: Identification of sinkhole
401 development mechanism based on a combined geophysical study in Nahal Hever South area
402 (Dead Sea coast of Israel). *Environmental Geology.*, 58, 1123-1141, 2009
- 403 Ezersky, M. and Frumkin, A.: Fault - Dissolution front relations and the Dead Sea sinkhole
404 problem. *Geomorphology.*, 201, 35-44, 2013
- 405 Fernandez, I., Olias, M., Ceron, J.C. and De la Rosa, J.: Application of lead stable isotopes to the
406 Guadiamar Aquifer study after the mine tailings spill in Aznalcollar (SW Spain), *Environ*
407 *Geol.*, 47, 197-204, 2005.
- 408 Fernandez-Galvez, J., Barahona, E., Iriarte, A. and Mingorance, M.D.: A simple methodology for
409 the evaluation of groundwater pollution risks, *Sci Total Environ.*, 378, 67-70, 2007.
- 410 Frumkin, A., Ezersky, M., Al-Zoubi, A., Akkawi, E. and Abueladas, A.-R.: The Dead Sea
411 sinkhole hazard: Geophysical assessment of salt dissolution and collapse. *Geomorphology.*,
412 134, 102-117, 2011
- 413 Goldscheider, N. and Bechtel, T.D.: The housing crises from underground – damage to a historic
414 town by geothermal drillings through anhydrite, Staufen, Germany. *Hydrogeology Journal.*,
415 17, 491-493, 2009
- 416 Gao, W.D.: Application of Entropy Fuzzy Discriminating methods in Distinguishing Mine



- 417 Bursting Water Source, Mining Safety & Environmental Protection., 39, 22-24, 2012.
- 418 Gutierrez, F., Parise, M., De, Waele, J. and Jourde, H.: A review on natural and human-induced
419 geohazards and impacts in karst. Earth Science Reviews., 138, 61-88, 2014
- 420 Hao, B.B., Li C. and Wang C.H.: Application of grey correlation degree in the identification of
421 sources of mine water bursting, China Coal., 36, 20-22, 2010.
- 422 Hu, W.W., Ma, Z.Y., Cao, H.D., Liu, F., Li, T. and Dou, H.P.: Application of Isotope and
423 Hydrogeochemical Methods in Distinguishing Mine Bursting Water Source, Journal of Earth
424 Sciences and Environment., 32, 268-271, 2010.
- 425 Houben, G.J., Sitnikova, M.A. and Post, V.E.A.: Terrestrial sedimentary pyrites as a potential
426 source of trace metal release to groundwater – A case study from the Emsland, Germany,
427 Appl. Geochem., 76, 99-111, 2017.
- 428 Jiang, R.Z. and Jiang T.X.: Present Development and Prospecting of Hydraulic Fracturing
429 Technology, Oil Drilling & Production Technology., 26, 52-57, 2004.
- 430 Kotwica, K.: Scenarios of technological development of roadways mining in polish coal mines
431 conditions, Gospod Surowcami Min., 24, 139-152, 2008.
- 432 Kang, X.B., Hu, X.W. and Xie, H.Q.: Numerical simulation on the influence of the groundwater
433 flow field during tunneling, Advanced Materials Research., pp. 1230-1233, 2012.
- 434 Lin, Y.X.: The History of Science & Technology of well salt in China, Sichuan Science and



- 435 Technology Pres, Chengdu, 1987.
- 436 Li, D.D. and Zhou, Z.A.: Possibility of corrosion failure of concrete shaftwall due to water
437 infiltration, Journal of China Coal Society., 21, 158-163, 1996.
- 438 Liu, H., Yang, T., Zhu, W. and Yu, Q.: Numerical analysis of the process of water inrush from the
439 12th coal floor FANGEZHUANG coal mine in China, Controlling Seismic Hazard and
440 Sustainable Development of Deep Mines: 7th International Symposium on ROCKBURST
441 and Seismicity in Mines (RASIM7)., 1&2, 1381-1386, 2009.
- 442 Lu, J.T.: Recognizing of Mine Water Inrush Sources Based on Principal Components Analysis
443 and Fisher Discrimination Analysis Method, China Safety Science Journal., 22, 109-115,
444 2012.
- 445 Lollino, P., Martimucci, V. and Parise, M.: Geological survey and numerical modeling of the
446 potential failure mechanisms of underground caves. Geosystem Engineering., 16, 100-112,
447 2013
- 448 Liu, R.Z., Liu, J., Zhang, Z.J., Borthwick, A. and Zhang, K.: Accidental Water Pollution Risk
449 Analysis of Mine Tailings Ponds in Guanting Reservoir Watershed, Zhangjiakou City, China,
450 Int. J. Environ. Res. Public Health., 12, 15269-15284, 2015.
- 451 Lee, H., Choi, Y., Suh, J. and Lee, S.H.: Mapping Copper and Lead Concentrations at Abandoned
452 Mine Areas Using Element Analysis Data from ICP–AES and Portable XRF Instruments: A



- 453 Comparative Study, *Int. J. Environ. Res. Public Health.*, 13, 384, 2016.
- 454 LeDoux, T.M., Szykiewicz, A. and Faiia, A.M.: Chemical and isotope compositions of
455 shallowgroundwater in areas impacted by hydraulic fracturing and surface mining in the
456 Central Appalachian Basin, Eastern United States, *Appl. Geochem.*, 71, 73-85, 2016.
- 457 Ma, L. and Qian, J.Z.: An approach for quickly identifying water-inrush source of mine based on
458 GIS and groundwater chemistry and temperature, *Coal Geology & Exploration.*, 42, 49-53,
459 2014.
- 460 Namin, F. S., Shahriar K., Bascetin A. and Ghodsypour S.H.: Practical applications from
461 decision-making techniques for selection of suitable mining method in Iran, *Gospod*
462 *Surowcami Min.*, 25, 57-77, 2009.
- 463 Parise, M., and Gunn, J.: Natural and anthropogenic hazards in karst areas: Recognition, Analysis
464 and Mitigation. *Geol. Soc. London*, sp. publ. 279, 2007
- 465 Parise, M. and Lollino, P.: A preliminary analysis of failure mechanisms in karst and man-made
466 underground caves in Southern Italy. *Geomorphology.*, 134, 132-143, 2011
- 467 Parise, M., Closson, D., Gutierrez, F. and Stevanovic, Z.: Anticipating and managing engineering
468 problems in the complex karst environment. *Environmental Earth Sciences.*, 74, 7823-7835,
469 DOI :10.1007/s12665-015-4647-5, 2015
- 470 Qiu, Z.Y.: Mechanism analysis of surface collapse in the area of solution salt mining, *Journal of*



- 471 Safety Science and Technology., 7, 27-31, 2011.
- 472 Robins, N.S.: Groundwater quality in Scotland: major ion chemistry of the key groundwater
473 bodies, *Sci Total Environ.*, 294, 41-56, 2002.
- 474 Ramadas, M., Ojha, R. and Govindaraju, R.S.: Current and Future Challenges in Groundwater. II:
475 Water Quality Modeling, *J. Hydrol. Eng.*, 13, 132-140, 2015.
- 476 Staudtmeister, K. and Rokahr, R.B.: Rock Mechanical Design of Storage Caverns For Natural
477 Gas in Rock Salt Mass, *Rock Mech&Min.Sci.*, 34, 3-4, 1997.
- 478 Shao, A.J., Huang, Y. and Meng, Q.X.: Numerical Simulation on Water Invasion of Coal Mine,
479 *Applied Mechanics and Materials.*, pp. 1112-1117, 2013.
- 480 Shi, T.T., Chen, Z.H. and Luo, Z.H.: Mechanism of groundwater bursting in a deep rock salt mine
481 region: a case study of the Anpeng trona and glauber salt mines, China, *Environ Earth Sci.*,
482 68, 229-239, 2013.
- 483 Vigna, B., Fiorucci, A., Banzato, C., Forti, P. and De Waele, J.: Hypogene gypsum karst and
484 sinkhole formation at Moncalvo (Asti, Italy). *Z. Geomorphol.*, 54, 285-308, 2010
- 485 Wang, J.M.: A Preliminary Study on the Characteristics and Conditions of forming Anpeng Trona
486 deposits, *Petrol Explor Dev.*, 5, 93-99, 1987.
- 487 Waltham, AC. And Fookes, PG.: Engineering classification of karst ground conditions. *Quarterly*
488 *Journal of Engineering Geology and Hydrogeology.*, 36, 101-118, 2003



- 489 Wei, Y.N.: Research and Application of Hydro-geochemical Simulation, Journal of Water
490 Resources and Water Engineering., 21, 58-61, 2010.
- 491 Wu, Q., Li, B. and Chen, Y.: Vulnerability Assessment of Groundwater Inrush from Underlying
492 Aquifers Based on Variable Weight Model and its Application, Water Resour Manag., 30,
493 3331-3345, 2016.
- 494 Xu, H. and Li, H.S.: Study on CaSO₄ crystallization process and its influential factors, Industrial
495 Water Treatment., 5, 67-69, 2011.
- 496 Yang, Y.H.: Gypsum mineral dissolution kinetics, M.D. thesis, China University of Geosciences,
497 Wuhan, China, 2003.
- 498 Yuan, W.H. and Gui, H.R.: The Characteristics of Geothermal Temperature and Its Application in
499 Distinguishing the Source of Water in Ren Lou Mine, Journal of Anhui University of Science
500 and Technology (Natural Science)., 25, 9-11, 2005.
- 501 Zhou, W. and Beck, B.F.: Engineering issues on karst. In: P. van Beynen (Ed), Karst Management.
502 Springer, Dordrecht, pp. 9-45, 2011



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.



Fig.1



Fig.2

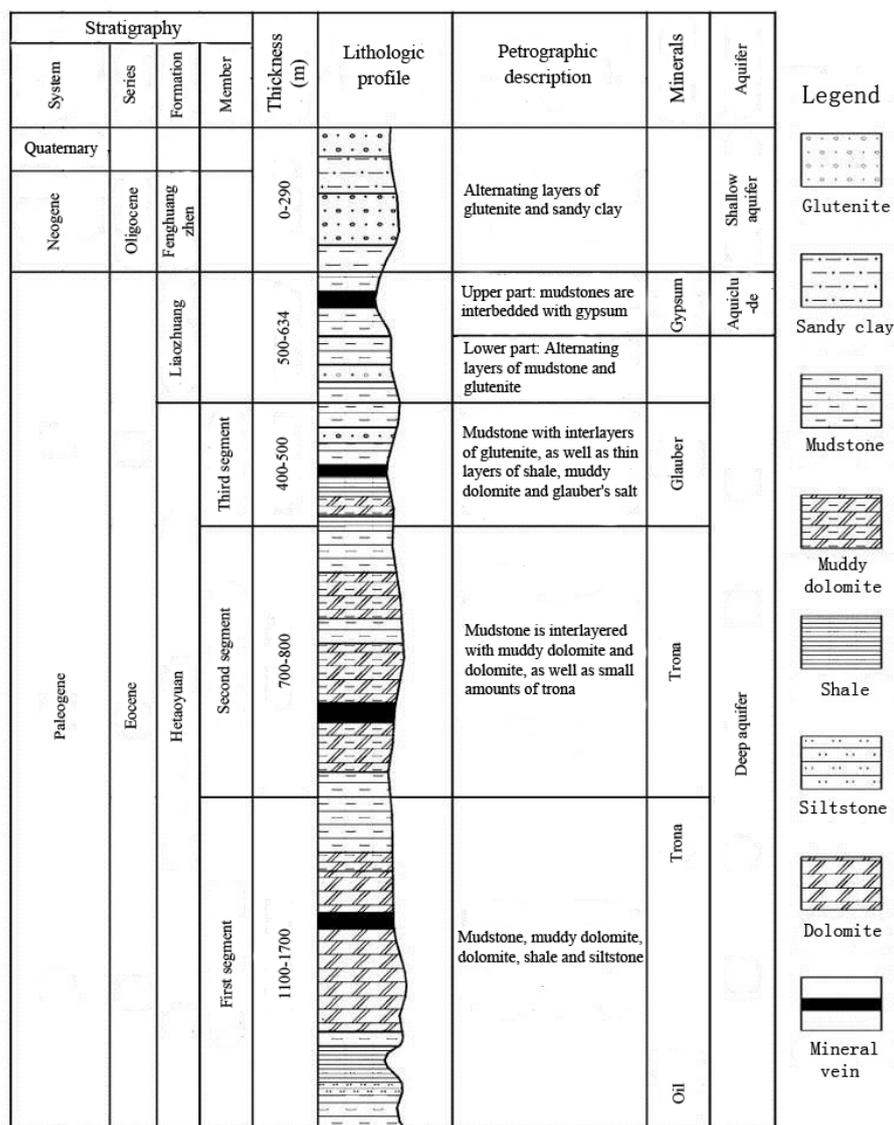


Fig.3

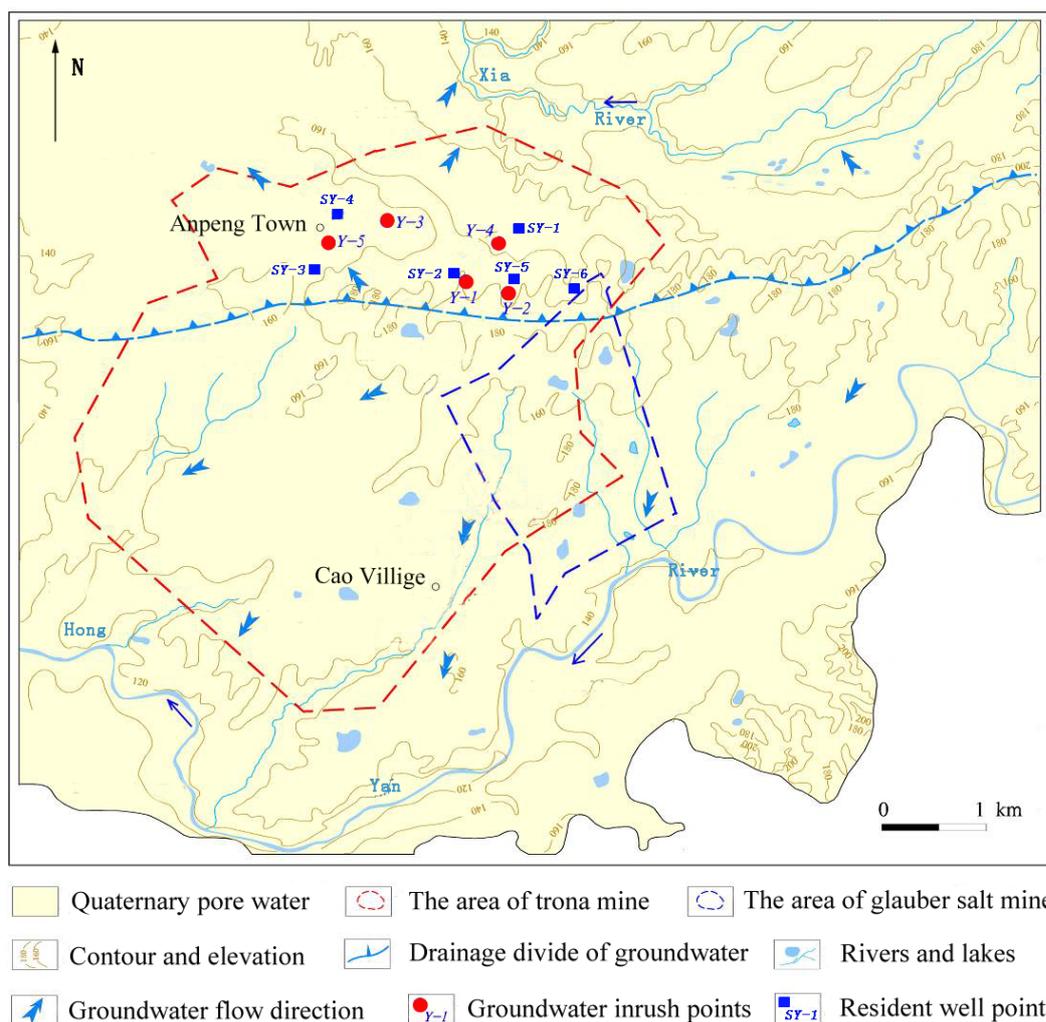


Fig.4

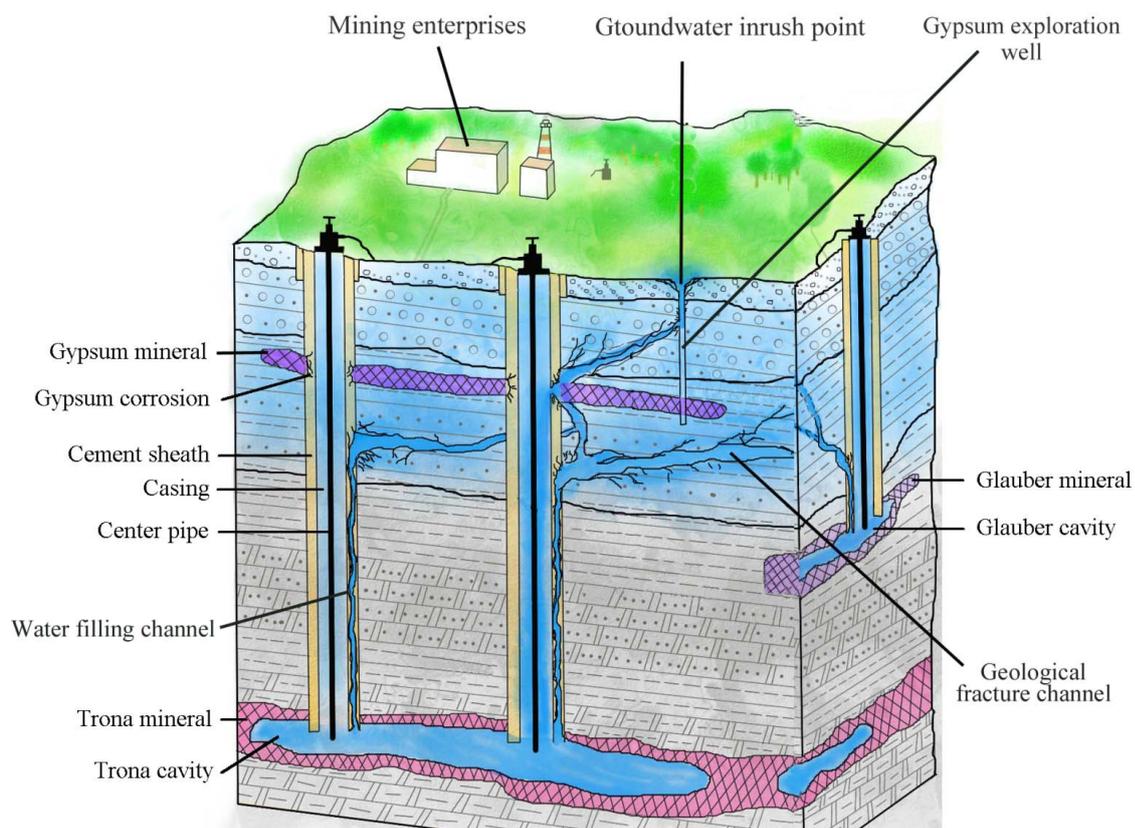


Fig.5



Table 1 Initial data of trona brine and background value of groundwater for PHREEQC simulation

Type	Temperature (° C)	pH	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
							(mg/L)		
Trona brine	70.0	10.8	85880	5.0	1.0	3819	206.0	104721	4565
Background value of groundwater	14.1	7.5	38.76	67.10	23.88	12.46	39.31	386.87	0.00



Table 2 Chemical composition of groundwater from inrush hazard points and surrounding resident wells

Source	Point	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	Salinity	Depth
		(mg/L)								(m)
Groundwater from inrush hazard points	Y-1	447.30	91.2	74.68	171.18	278.55	1488.89	0.00	1807.35	330.55 ~ 430.2
	Y-2	524.50	89.34	75.32	153.97	298.88	1525.00	0.00	1904.51	
	Y-3	1132.00	146.6	158.30	125.56	4296.44	1012.93	0.00	6365.37	
	Y-4	322.12	98.67	123.88	210.78	346.55	1122.77	0.00	1663.38	
	Y-5	50300.00	12.23	53.21	3813.80	12858.63	81309.15	27159.0	107692.4	
Groundwater from resident wells around the inrush points	SY-1	46.28	76.76	17.29	64.3	14.58	319.03	0.00	378.73	10.00
	SY-2	28.37	98.02	27.46	26.16	10.38	453.84	0.00	417.31	
	SY-3	43.14	46.2	14.42	31.02	117.12	319.03	0.00	316.26	
	SY-4	118.53	278.4	72.3	425.23	175.96	568.52	0.00	1354.68	
	SY-5	31.67	95.51	19.22	53.93	22.59	351.97	0.00	398.9	
	SY-6	36.77	68.82	19.6	18.51	21.55	340.38	0.00	335.43	



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

Conditions	Mixed proportion with shallow groundwater	Na ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Trona brine unmixed or mixed with different proportion of shallow groundwater after flowing through the mineral layer (simulation results)	Unmixing	87147.00	301.08	3880.15	68659.20	5.06
	1:1	48093.00	280.00	2145.62	37900.80	9.39
	1:2	33235.00	184.72	1485.68	26188.80	13.97
	1:10	9586.40	148.28	436.30	7561.92	57.95
	1:100	1098.25	90.40	141.63	873.89	306.34
	1:200	571.78	69.60	118.56	459.17	382.17
	1:500	252.77	68.32	104.60	207.84	453.66
Water quality test results in five water inrush hazard points	1:1000	144.81	67.52	99.94	105.12	481.60
	Y-1	447.30	91.20	171.18	276.55	1488.89
	Y-2	524.50	89.34	153.97	298.88	1525.00
	Y-3	1132.00	146.60	125.56	4296.44	1012.93
	Y-4	322.12	98.67	210.78	346.55	1122.77
	Y-5	50300.00	12.23	3813.80	12858.63	81309.15