Original Research Paper

Study of Cole-Cole Complex Resistivity Model for Chrome-Contaminated Soil

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ABSTRACT

Complex resistivity method is used to measure the concentration distribution of chromium salt in the chrome-contaminated sites. Both, the salt concentration and moisture content could affect the measurement results, so a theoretical model is needed to distinguish the salt concentration and moisture content. The results of soil electrical test show that the soil has not only resistance character, but also capacitance character. The Cole-Cole complex resistance model of rock is used as the complex resistance model of soil. Cole-Cole model has four parameters: resistivity, time factor, charge rate and frequency factor. The math relation between soil physical parameter and measured resistivity is based on the solution resistivity. The math relation between soil physical parameter and time factor is derived from the double layer deformation, which includes electromagnetic field theory and the double-gel plate model. Finally, the theoretical derivation is compared with the experimental data to verify its accuracy.

INTRODUCTION

With the resistivity method to detect chrome-contaminated sites, the soil temperature, soil type, moisture content, porosity and contaminants can directly affect the conductivity of the soil, resulting in a diversity of resistivity data analysis, and these data cannot accurately describe the change of chromium contamination (Liu et al. 2009, Luo et al. 2010). Experimental study of the electrical characteristics of the existing chrome-contaminated soil shows that the soil has not only the resistance characteristics, but also the capacitance characteristics (Liu 2010a). The soil electrical double layer is the reason of capacitance characteristics of the soils (Khamzin et al. 2010, Flekkoy et al. 2010). With the help of complex resistivity method, the Cole-Cole mathematical model is discussed on the basis of existing theory to distinguish the difference between salt concentration and moisture content (Liu 2010b).

MATERIALS AND METHODS

Complex resistivity method, used to detect contamination, reflects the electrical properties of the soil, including soil solution conductivity, particle conductivity and capacitance caused by deformation of double electric layer. Complex resistivity contamination detection method initially was applied in the field of geophysical studies. According to the experimental verification, Dias model and Cole-Cole model could reflect the induced polarization response of rocks and minerals much better in those variety models. Because Cole-Cole model has certain advantages in fitting accuracy and

the physical meaning of the parameters, it will be used as the preferred soil complex resistivity model. Schematic model is shown in Fig. 1, where R_0 is the DC resistance without taking into account the effect of induced polarization, and Ω is unit; R_1 is the total resistance of the solution and solid particles in the block passage, and Ω is unit; capacitor X has unit F; frequency factor c is dimensionless; i is the imaginary unit; ω is the angular frequency (Stefan et al. 2014, Tarasov et al. 2013).

So, we have the expression of Cole-Cole model for soil complex resistivity in the formula. ρ_0 is the DC resistivity derived from R_0; charging rate $m = R_0/(R_0 + R_1)$ is dimensionless; the time constant $\tau = X.(R_1/m)$ has unit s.

$$\rho = \rho_0 \left[1 - m \left(1 - \frac{1}{1 + (i\omega\tau)^c} \right) \right] \qquad ...(1)$$

In the above model, m and c are mainly determined by the nature and porosity of the soil particles, and not sensitive to the external factors. ρ_0 and τ is determined by the soil properties and soil solution together, which makes ρ_0 and τ is a function of ion concentration and moisture content. Therefore, this article will focus on the derivation of ρ_0 and τ from ion concentration and water content of the soil. Each parameter distribution range of complex resistivity is roughly as: $m = 0 \sim 0.98$, $\tau = 10E\text{-}3 \sim 5 \times 10E+3s$, $c = 0.1 \sim 0.6$, $\rho_0 = 10E\text{-}4 \sim 10E+5\Omega.m0$

Derivation of DC resistivity ρ_0: According to Archie formula (1),

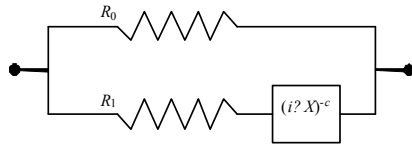$$\rho_0 = K\phi^{-m} S_r^{-n} \rho_W \qquad ...(2)$$

Fig. 1: Cole-Cole model for soil complex resistivity.

Fig. 2: EDL capacitance.

The soil resistivity can be calculated based on the porosity ϕ, saturation S_r, resistivity ρ_w of the solution. K, m and n are the correction coefficients about soil. The relationship among porosity, saturation and water content can be expressed as $S_r = W_c/\phi$, wherein W_c is the volume-based water content; solution resistivity can be calculated based on the solution's molar conductivity $\rho_w = 1/\kappa = (\Lambda n^0)$, in which, κ is expression manner of the conductivity in physics and chemistry, Λ refers to the solution's molar conductivity, and n^0 displays the molar concentration of ions. Then the formula (2) is translated into:

$$\rho_0 = K\phi^{n-m}W_c^{-n}\left(\Lambda n^0\right)^{-1} \qquad ...(3)$$

The relationship between the concentration and quality-based concentration of chromium (Cr) ions is:

$$n^0 = \frac{\lambda^p \gamma}{52 \times W_c} \qquad ...(4)$$

Wherein λ means quality content (mg/kg) of Cr, γ means soil bulk density (g/cm³); formula (3) can be translated into the following one when formula (4) is integrated:

$$\rho_0 = \frac{52K\phi^{n-m}}{\Lambda \lambda^p \gamma W_c^{n-1}} \qquad ...(5)$$

Derivation of time factor τ: In Cole-Cole model, X is the dielectric constant with F·m⁻¹ dimension and the capacitive reactance is the result of electric double layer (EDL) of soil (Li 1999). Differential capacitance C is another parameter describing EDL. Capacitor is generally defined as the electric charges stored between the two layers separated by dielectric medium divided by the inter-layer voltage; or it is also defined as the electric charges stored between the two layers divided by the inter-layer voltage change ratio. The latter is referred to as "differential capacitance", but usually the stored charge is proportional to the voltage, so that the two definitions are equivalent. In addition to the usual capacitor form, there is a parallel plate capacitor. However, this definition is meaningful when applied in any two fields, such as spheres unnecessarily with the same size. Differential capacitance between the spheres is the opposite charges ± q. Differential capacitance in the second form refers to a single isolated conductor, usually seen in static charges. The absolute potential depends on the selected reference, also known as self-capacitance defined by the following formula:
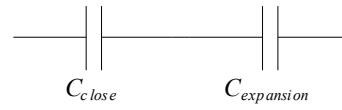
$$C_G = \frac{\partial \sigma}{\partial \varphi} \qquad ...(6)$$

Where φ_s represents the electric potential on Stern surface, and the EDL capacitance can be calculated according to the following formula (3) and the smaller $C_{expansion}$:

$$\frac{1}{C_G} = \frac{d\varphi}{d\sigma} = \frac{d\left(\varphi_0 - \varphi_s\right)}{d\sigma} + \frac{d\varphi_s}{d\sigma} = \frac{1}{C_{close}} + \frac{1}{C_{expansion}} \approx \frac{1}{C_{expansion}}$$
$$...(7)$$

EDL capacitance can be calculated with the double-colloid plate (Fig. 2); formula (7) can be translated into the following one when formula (6) is integrated

$$C_G = -\frac{\Phi}{W_c}\sqrt{\frac{\varepsilon n^0 (ze')^2}{2\pi kT}}\left(\sinh \frac{ze'\varphi_S}{2kT}\right)\left(2\cosh \frac{ze'\varphi_S}{2kT} - 2\cosh u\right)^{\frac{1}{2}} \qquad ...(8)$$

The molar concentration of ions can be converted into quality-based content.

$$C_G = \Phi ze'\sqrt{\frac{\varepsilon n^0 \gamma \lambda}{104\pi kTW_c^3}}\left(\sinh \frac{ze'\varphi_S}{2kT}\right)\left(2\cosh \frac{ze'\varphi_S}{2kT} - 2\cosh u\right)^{\frac{1}{2}} \qquad ...(9)$$

Where, z is the price of negative ion, and sodium chromate solution value is 2; e' is the electron charge, 1.6E-19 Coulomb; n^0 refers to the concentration of ions (mol·L-1); λ is the quality-based content of Cr (mg/kg); ε is the dielectric constant (=3); k is the Pohl Seidman constant, 1.3807E-23 J, K-1; T refers to thermodynamic temperature; φ is the electric potential (= 40E-3); Φ is porosity; W_c is moisture content. In the circuit model, X is equal to self-capacitance in value. So we get τ in the definition of mathematical model as:

$$\tau = C_G\left(\frac{\rho_0}{m}\right)^{\frac{1}{c}} \qquad ...(10)$$

RESULTS AND DISCUSSION

In order to verify the correctness of the formula of soil colloid's EDL capacitance, the theoretical calculated result and the experimental measurement are comparatively analysed, with four pollution concentration values, 50ppm, 250ppm, 1000ppm and 4000ppm with moisture content of 0.1 and 0.2, as examples; the actually measured electrical resistivity is regarded as DC electrical resistivity, and the charge rate and frequency factor measured in experiment are respectively
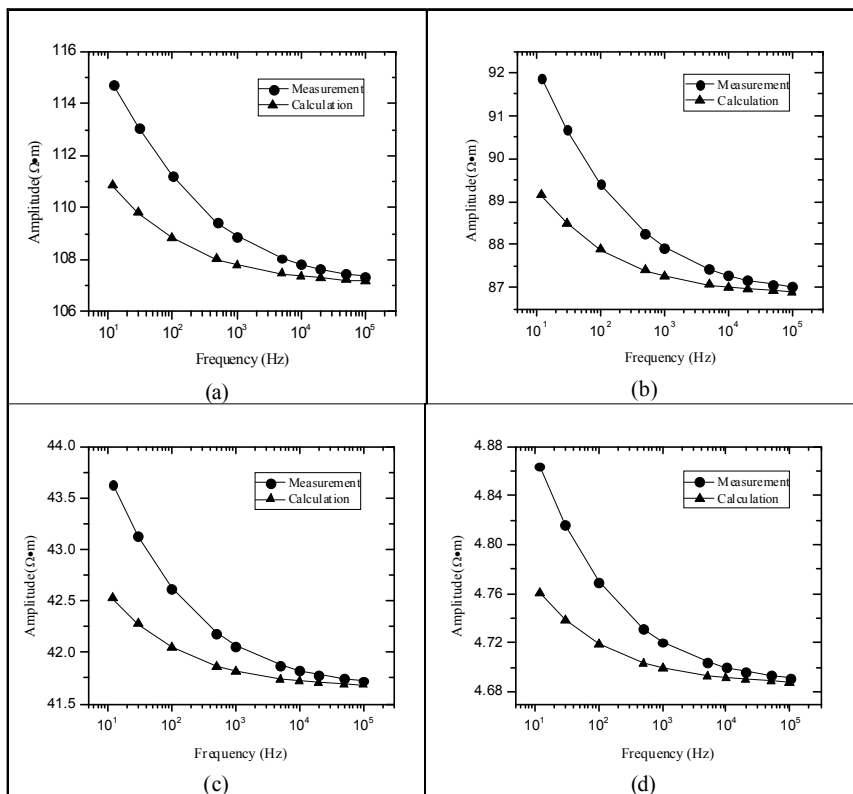
Fig. 3: Comparison of measured amplitude and calculated amplitude of complex resistivity of samples with moisture content 0.1; (a) The concentration of chromium: 50ppm; (b) The concentration of chromium: 250ppm; (c) The concentration of chromium: 1000ppm; (d) The concentration of chromium: 4000ppm.

0.138 and 0.4. Their comparison is shown in Figs. 3 and 4.

As is shown in Figs. 3 and 4, about the amplitude of Cr concentration in soil samples with different moisture contents, the actual measured value is just slightly different from the theoretically calculated value, which can be explained from two perspectives:

1. Small difference: When theoretically calculating the mathematical formula of Cole-Cole model, measured value of DC resistivity is adopted, which reduces the difference between the theoretical calculation and actual measurement to certain extent.

2. Existence of difference: The difference is mainly caused by the time factor τ. That is, large difference arises in the middle frequency band, while the two tend to be equal at high frequency band. The difference remains within 2%, thus theoretical calculation formula can be directly used, without the necessity to introduce correction coefficient.

According to the above analysis, the theoretical reasoning of EDL self-capacitance and time factor τ based on colloid plate model actually agrees with the measurement. In Formula (5), the mass-based content of Cr and moisture content index are consistent, while in formula (9) they are inconsistent, which explains the two different soil samples with the same DC resistivity and different complex resistivity rate amplitudes, and provides theoretical basis for the distinction in the effects between Cr pollution concentration and moisture content.

CONCLUSIONS

In this study, Cole-Cole circuit model is selected as soil's complex resistivity rate model, based on which the resistance and capacitance characteristics of soil are discussed. According to the Archie formula, the DC resistivity, playing dominant role in electric conduction process, is calculated for the conclusion of soil's complex resistivity rate. It is the soil's EDL deformation that causes the soil's capacitance; then electric charge density distribution formula in EDL is concluded based on the double colloid plate model, then accordingly the partial derivative of potential is reached, and the EDL capacitance parameter with capacitive characteristics of soil's complex resistivity is calculated. The final results and the experimental data are comparatively analysed, showing the deviation less than 2%, which confirms that the
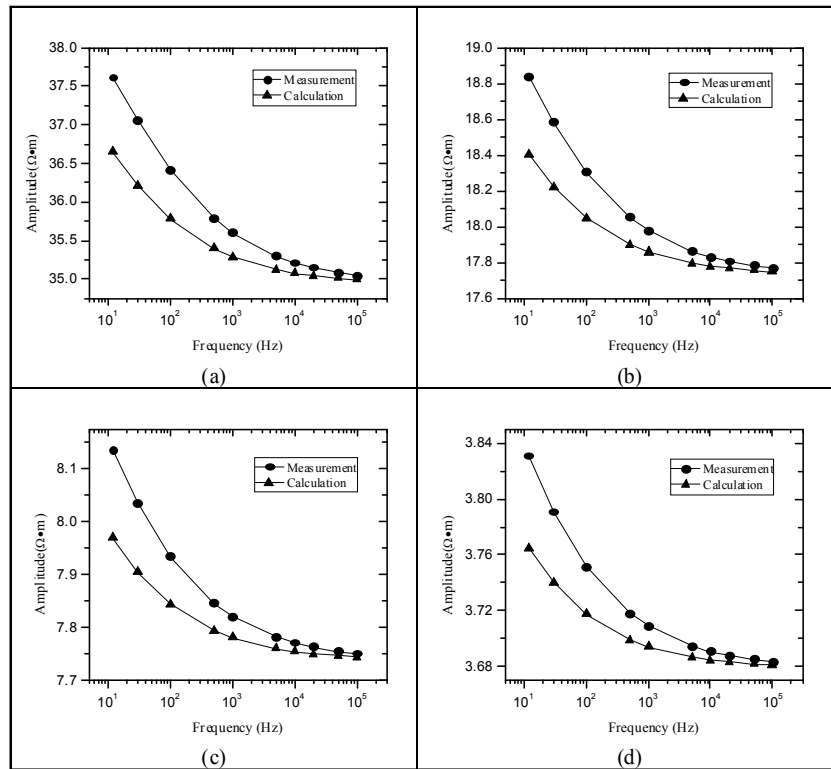
Fig. 4: Comparison of measured amplitude and calculated amplitude of complex resistivity of samples with moisture content 0.2; (a) The concentration of chromium: 50ppm; (b) The concentration of chromium: 250ppm; (c) The concentration of chromium: 1000ppm; (d) The concentration of chromium: 4000ppm.

Cole-Cole model can accurately describe the soil's resistance.

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