

**ON THE SEVENTIETH ANNIVERSARY OF THE “SUSPENSION EFFECT”:  
A REVIEW OF ITS INVESTIGATIONS AND INTERPRETATIONS**

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**Abstract**

A short critical review of Suspension Effect (SE) studies since its naming up to the present and the causes of the lack of a consensus about its origin and nature are given.

An argued (operational) SE definition and an interpretation based on this are presented considering the SE as the sum of two effects, one as the occurrence of the irreversible mixed potential of the indicator electrode and one as the anomalous liquid junction potential at the contact of the reference electrode salt bridge with the suspension. In systems subject to the SE the ion activities are not determinable rigorously; however their estimation could be useful as shown by "soil pH" determinations.

**Introduction**

The seventieth anniversary of the Suspension Effect (SE), a troublesome phenomenon in potentiometry, means seventy years since the phenomenon received its name,<sup>1,2</sup> and also the period during which no consensus about its cause and nature was achieved, in spite of the intensive efforts of researchers. This following chronological review and analysis of the SE investigations should contribute to this aspiration.

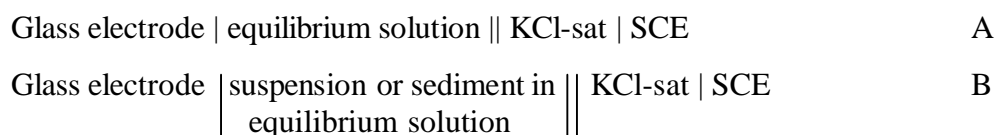
Though the SE is a common phenomenon in the potentiometry of suspensions, the following review refers above all to electrometric pH measurements.

**Period from 1930 to 1970**

The most extensive monograph about the SE since its naming up to 1975 was published by Chernoberezhskii in “Surface and Colloid Science”.<sup>3</sup> Difficulties in pH measurements, and in inversometric methods applied to soil suspensions, were mentioned before 1920.<sup>3,cit 2-26</sup> For the phenomenon of the voltage dependence of a pH galvanic cell

on the particle concentration in the same equilibrated suspensions, Pallmann and Wiegner in year 1930 introduced the term “Suspension Effect”.<sup>1,2</sup>

The subsequent operational SE definition means “the difference in emf obtained in the conventional determination of the pH in a suspension and in its equilibrium solution”, (Overbeek 1953). The simple schemes of the corresponding pH cells are as follows:



where SCE means the saturated calomel electrode. Neither of the two cells includes the phase boundary between the sediment and the equilibrium solution, or any corresponding potential jump.

Both original authors<sup>1,2</sup> considered the SE to be a consequence of the greater concentration of H<sub>3</sub>O<sup>+</sup> counterions in the double layer of charged particles (Schwarmionen) than in the equilibrium solution, influencing the potential when in contact with the indicator electrode. This contribution to the SE arising at the indicator electrode interface (SE of the first kind, SE I) was later termed the “Pallmann-Wiegner SE” (PWSE).

Because the above consideration was not consistent with the second law of thermodynamics (according to which the potential values of the indicator electrode must be equal in every part of an equilibrated system), in the year 1934 Nikolsky proposed a new interpretation of the SE,<sup>4</sup> supported by other Russian scientists<sup>3,cit33-38</sup> and based on the “Donnan theory of membrane equilibrium”. The SE was regarded as the “Donnan potential” at the sediment/ultrafiltration interface of the *combined suspension system*, (where the suspension (or sediment) and the separated ultrafiltration (equilibrium solution) are in electrical and physical contact), as was described early by Hill.<sup>5</sup> Many researchers made unfounded use of this interpretation in discussions of the SE. But regarding the above definition of the SE (cells A and B) the contact between the sediment and equilibrium solution established in the combined system is neither necessary nor essential for the SE, because the measured voltages of both cells are independent of this

contact. The Donnan potential is not present in either cell and cannot contribute to or be identical with the SE, exactly contrary to what some authors assert.

Since the often cited Donnan equilibrium and Donnan potential are mentioned above for the first time in this review and equating them with the SE is rejected, it must be emphasized that the Donnan equilibrium, established not at the sediment/equilibrium solution interface (the optical boundary!) but at the interfaces between the single charged particles and the surrounding solution, is itself indirectly the essential condition for occurrence of the SE,<sup>3,p.401</sup> which is also in accordance with the “theory of membrane (Donnan) equilibrium“.<sup>8</sup> The particles mentioned can be e.g.

- a) ion exchanger beads,<sup>6</sup>
- b) hydrated SiO<sub>2</sub> -particles with dissociated counterions<sup>3</sup> or
- c) particles with adsorbed ions<sup>7</sup> in a solution.

The Donnan partitioning of ions between the particles and the surrounding solution is also the cause of the often underestimated differences in the electrochemical behaviour of true solutions and suspensions.

In each equilibrium system of suspensions the electrochemical potential ( $\tilde{\mu}_{H^+}$ ) is equal at all points of the system. Therefore, if the electric potential ( $\phi_x$ ) changes with the distance  $x$  from the surface of the charged particle, the pH value at the distance  $x$  ( $\text{pH}_x$ ) also changes. Because

$$\tilde{\mu}_{H^+} = \tilde{\mu}_{H^+}^0 + kRT \log(a_{H^+})_x + F(\phi_x), \text{ it follows that } \tilde{\mu}_{H^+}/F = \tilde{\mu}_{H^+}^0/F - (kRT/F) \text{pH}_x + \phi_x$$

where  $\tilde{\mu}_{H^+}^0$  is the standard electrochemical potential,  $(a_{H^+})_x$  the activity of hydrogen ions at the distance  $x$ , and  $K$ ,  $R$ ,  $T$ ,  $F$  have their common meanings. The pH electrode does not respond to these changes of  $\text{pH}_x$ , though the electrode penetrates the particle double layers, until  $\tilde{\mu}_{H^+}$  is throughout equal, because its potential  $E_{\text{ind}}$  is determined by  $\tilde{\mu}_{H^+}$ .

If, however,  $\tilde{\mu}_{H^+}$  changes due to whatever cause, e.g. because of the overlapping of the double layers of the particles and that of the electrode,<sup>9,ch.7; 10,chp.71</sup> this means a local equilibrium change perceived by the pH electrode, which also changes its pH indication. The other parts of the system remain in equilibrium. If the reestablishment of

the former equilibrium proceeds very slowly, a steady state process may be set up for a long time, as experiments show. To visualise the particles surrounded by counterions, they could be regarded as labile closed “reservoirs of counterions”, which open where and when the equilibrium (or  $\tilde{\mu}_{H^+}$ ) changes, and set the counterions free in their proximity.

In the year 1950 Jenny proposed a new interpretation of the SE,<sup>11</sup> based on the known fact that in potentiometric measurements liquid junctions occur, which are the seats of the irreversible liquid junction- ( $E_{lj}$ ) or diffusion- ( $E_{dif}$ ) potentials. If reference electrodes with salt bridges are used, from which the  $KCl_{sat}$  diffuses into a true solution,  $E_{dif}$  decrease to the very small values, but they may increase much when  $KCl_{sat}$  diffuses among the suspension particles, partly because of the ion exchange of KCl with the counterions, partly due to the changes of the ion transport numbers in “the high electric fields around the particles”. Jenny assumed that the difference between  $E_{dif}$  in the suspension (or sediment) and the equilibrium solution is the sole cause of the SE, which can be regarded as the SE of the second kind, SE II.

Many authors commented on Jenny’s SE explanation (e.g. Erikson,<sup>3,cit 55</sup> Marshall,<sup>3,cit 57</sup> Sollner<sup>3,cit 63</sup> and others) until in 1953 Overbeek published a compromise treatment of the SE, based on thermodynamics.<sup>12</sup> He started from the valid SE definition, but he later developed his SE interpretation on the basis of the *combined suspension system*, which included the sediment/equilibrium solution interface. The author denied that the SE arises from the interface of the pH electrode (PWSE) and he equated the SE completely with the “Donnan emf” and presented an equation for its estimation. Later the validity and the (dis-)agreement of Overbeek’s assumptions with experiment was the theme of many publications (Bower<sup>3,cit.69</sup>, Tschappek,<sup>3,cit. 70,71</sup> Kahlweit,<sup>3,cit 68</sup> Bloksma,<sup>13</sup> including critical evaluations and additions (Honig,<sup>3,cit 88</sup> Peech et al.,<sup>3,cit 87</sup> Spiegler,<sup>3,cit 148</sup> Olsen, Robbins<sup>3,cit 86</sup> and others).

Overbeek’s explanation was an important milestone of the SE study. Therefore SE II was later called (not quite consistently with Overbeek’s SE concept), “Overbeek’s SE” (OSE).<sup>14</sup> Equating the SE with the “Donnan emf” comprises besides both liquid junctions (the sole cause of the SE according to Jenny’s assumption!) also the potential

jump at the sediment/equilibrium solution interface (also named the “Donnan potential” and declared by Nikolsky as the sole cause of the SE), and so represents a combination of the last two above mentioned (Jenny’s and Nikolsky’s) SE interpretations. However, regarding the SE definition formulated by Overbeek himself,<sup>12</sup> his SE interpretation is not valid, as explained above. The same SE concept was also advocated in Overbeek’s publication of 1956<sup>10</sup> and was proposed by IUPAC in the year 1972<sup>15</sup> misleadingly as the definition of the SE.

Because in addition no consensus was attained about the meaning of commonly measured soil pH values, experts presented special routine methods for this pH determination, used to the present day. Besides direct measurement in wet soils or soil suspensions in water, in solutions of KCl and CaCl<sub>2</sub>, equilibrium solutions separated from soil were used for pH measurement. These determinations, which have to be carried out exactly following the instructions, offer useful, comparable information about soils, but they are not determined with regard to the definition  $\text{pH} = -\log a_{\text{H}^+}$ , except when performed in equilibrium solution as operational pH values.

#### Period between 1970 and 1995

No publication was found in the literature between 1930 and 1970 referring to the potential difference of a pH electrode when applied in sediment and in its equilibrium solution of a *combined suspension system*. In suspensions (or in slurries) of rough grained ion exchangers, usually showing very high SE values (and therefore very often applied for the study of SE), this potential difference should not even be expected, unlike many other suspensions.

As early as in 1972 Milička<sup>16,17</sup> in addition to measurements of the SE II in *combined suspension systems* of ion exchangers, also published reliable, valid measurements of the SE I in *combined colloidal systems*, which he ascribed to processes on the pH indicator electrode, as Pallmann and Wiegner did, although unfortunately without a suitable explanation.

Similarly, in 1976 Schwabe<sup>18</sup> measured different potentials of the pH electrode when immersed in sediment and its equilibrium solution. He attributed this difference to the strongly polarised water around the suspension particles, which results in an increased

local activity of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions (SE I!). He also found considerable diffusion potentials at the tips of the reference electrode in suspensions (SE II!), and he denied that the potential jump at the sediment/equilibrium solution interface was the cause of the SE. However, his explanation of the SE I is not valid for the same reason as given in the explanation of Pallmann and Wiegner.

Later publications<sup>16,17,18</sup> are important because they represent reliable cases of the SE I in equilibrated suspension systems, though the valid explanation of the phenomena was still the object of investigation and though the authors were exposed to the imputation of arguing for “perpetuum mobile”. Some other SE investigators considered that these measurements were not experimentally credible and were only a consequence of nonequilibrium in the systems.

Chernoberezhkii, who in his monograph about the SE<sup>3</sup> proposed some criteria for equilibrium in a combined suspension system, also advocated this opinion, but his propositions are neither convincing nor reliable. The monograph contains his own results about the SE, which is interpreted on the basis of the *combined system*<sup>3.p. 446</sup> and includes the sediment/equilibrium solution interface. Therefore his SE interpretation is not valid.

In the year 1983 an interesting study on the origin of the SE was published by Brezinsky.<sup>19</sup> According to him the SE should mean the Donnan potential at the sediment/supernatant interface. Therefore his explanation is also not valid.

Two years later, 1985, Yu published a new review of the SE within coverage of the routine applications of “ Ion- selective electrodes in soil chemical studies”.<sup>20</sup> He “ considers that in soil pH measurements both the calomel reference electrode and the glass electrode can contribute to the SE”. He was the third author in recent years to concede a SE of both kinds. The mechanism of SE I formation, as described by the author, does not guide the processes to the equilibrium electrode potential, “ to give the real pH of the soil”, as assumed. The not exactly specified “pH of the soil” is presented as being dependent on the manipulation procedure of pH measurement. Therefore his interpretation of SE I is not cogent. In what relates to the contribution of the reference electrode to the SE, the author agrees with Jenny’s explanation of the SE. He does not mention nor does he assume the Donnan potential as the origin of the SE.

In 1986 a discussion was presented<sup>21</sup> about “the electrostatic and thermodynamic analysis of SE potentiometry for compacted ion exchanger resin beads”, which should be applicable to the other suspensions. The already known views on the SE are discussed, which are similar to Brezinsky’s concept of the SE.<sup>19</sup> The main contribution to the SE is presented as the “phase boundary potential difference between supernatant and slurry phase”. Therefore this interpretation is not valid in view of the above mentioned reasons. Many other assumptions and assertions, which were not argued, diminish the persuasiveness of this paper.

A publication entitled “Suspension effect in potentiometry”,<sup>22</sup> treating the SE as two separate effects, appeared in 1989. It must be regarded from two points of view, firstly as discussing the cause and nature of the SE, and secondly as a promotion of the “chemical capacitor theory”, applied to the glass electrode. This second aspect does not belong to the field of discussion treated here. On the other hand, the interpretation of both kinds of SE as arising from particle adsorption, one at the glass electrode interface and the other “on the SCE tip opening” is not argued experimentally.

In spite of the increasing number of advocates of both kinds of contributions to the SE, some authors still persist in “conclusions, that the SE is exactly identical to the Donnan emf”<sup>23</sup> and others, that the SE is “determined solely by electric potential differences developed at the two liquid junctions, that involve KCl salt bridges”, one inserted in a suspension and the other in equilibrium solution.<sup>24</sup>

Taking into account the different views on the SE and the persistence of the early SE concepts, without willingness to find a consensus, one may understand why in 1994 a new formulation of the definition of the SE<sup>25</sup> was proposed, not in accordance with the early commonly accepted definition. In the “Abstract” of the publication “IUPAC Recommendations 1994” the assertion is made, that “IUPAC Recommendation 1975 has been corrected, using recent experimental and theoretical findings”. But in the new definition of the SE it is possible to see only slight modifications reflecting the contents of the article, mentioned above.<sup>21</sup>

### Period after 1995

A new approach to a resolution of the disputable assumptions and statements about the SE began 1986 with a study of the SE based above all on experiments, the results of which were published.<sup>14,26-31</sup> Their contents complement each other. Instead of an analysis of individual parts of the investigations, where some unreliable statements could possibly still be found, the final SE interpretation and its argumentation are presented.

The pH value measured in a suspension depends to a high degree on the measurement technique. Therefore knowledge and an understanding of the measurements are prior conditions for a valid interpretation of the SE.

For pH measurement in connection with the operational determination of the SE, a galvanic cell with a glass- and a reference- (e.g. SCE) electrode, both inserted first in the sediment and then in equilibrium solution, is commonly used. Other electrode couples can also be applied. The first step of the analysis of these cells is the determination of their detailed scheme.<sup>31</sup> These show that in these cells only two potential jumps can change, one at the glass electrode,  $E_{\text{ind}}$ , and the second,  $E_{\text{lj}}$ , where the tip of the reference electrode salt bridge makes contact with the medium. In neither cell does a sediment/equilibrium solution interface exist where a boundary potential could arise, being the partial or the only cause of the SE, as is assumed in many publications.<sup>44,15,19,21</sup> Because the single electrode potentials are not measurable, the *equilibrated combined systems* with the sediment/equilibrium solution interfaces were used for their evaluation.

The first possible cause of the SE is the change of the liquid junction potential,  $E_{\text{lj}}$ , the significance of which in pIon measurements of true solutions is known. Because an "ideal" reference electrode ( $E_{\text{lj}}=0$ ) is not known, reference electrodes with negligible  $E_{\text{lj}}$  are applied, e.g. the SCE, from which KCl solution flows into the measured medium. This is not a problem for true solutions, except in some extraordinary cases, but it could evoke a considerable "anomalous"  $E_{\text{lj}}$  when the reference electrodes are inserted into suspensions, or even when the tip of the salt bridge only approaches near to the sediment boundary, though it is not yet in contact with the particles.<sup>26</sup> If the direction of flow of



the KCl solution is reversed back into the salt bridge,  $E_{ij}$  decreases, but it is not well defined.<sup>30</sup>

It follows from experiments<sup>14,26,30,31</sup> that the anomalous liquid junction potential is a) the consequence of the KCl solution contacting the particles (ion exchange, change of the Debye - Hückel reciprocal length, double layer change of particles), b) dependent on the suspension liquid and c) dependent on the particle size and species. It does not depend on particle adsorption or contact with the salt bridge tip. The type of reference electrode separator is usually not important, except for its permeability to KCl solution.

If in suspensions an Ag/AgCl electrode is used directly, as a reference electrode without a salt bridge, even the dissolution of AgCl from the electrode surface and the subsequent diffusion of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions among the particles can change the cell potential and cause a (small) SE.<sup>27</sup>

The change of  $E_{ij}$  as a consequence of KCl solution outflow from a salt bridge among the suspension represents the SE II and is a systematic error of potentiometric measurements. It can be nearly eliminated in different ways:

- a) with a reference electrode constructed with two salt bridges in series, the final one being filled with an equilibrium solution of the measured suspension,<sup>14,26</sup>
- b) with the aid of filter paper strips, soaked in equilibrium solution, which make contact between the soil and the tip of the reference electrode,<sup>20</sup>
- c) by using the *combined suspension system* with the indicator electrode (e.g. glass electrode) inserted in the sediment and the salt bridge of the reference electrode in the equilibrium solution.<sup>14,20</sup>

These three SE II elimination procedures are meaningful and valid only if the boundary potential difference at the sediment/equilibrium solution interface is zero. The potential difference at this boundary, sometimes called the “fictitious membrane”, was often discussed with interesting results (e.g. in regard to the Donnan emf,<sup>10,12</sup> in Jenny’s SE interpretation,<sup>11</sup> in connection with the “leaky membrane potential” in suspensions,<sup>3</sup> etc). It is not measurable directly by experiment. Considering that the interface sediment/equilibrium solution is a very permeable (optical, not Donnan!) boundary between the particle sediment and the equilibrium solution, and that a Donnan potential

exists around each charged particle, (but which should result according to some authors in a potential jump on this fictitious membrane) and further, if the results of a step by step approach of one SCE toward and through the "fictitious" membrane<sup>26</sup> and the results of check experiments testing the change of membrane potentials caused by vigorous stirring of boundaries<sup>30,31</sup> are taken into account, it is possible to say that this potential difference is equal to zero, in agreement with theoretical calculations<sup>3, cit 88</sup> and with the views of some authors.<sup>24</sup>

The second possible cause of the SE is the potential change of the indicator (e.g. glass) electrode, when this is inserted in the sediment. Its direct measurement is not possible. Therefore experiments were performed in equilibrated *combined systems*, where the electrochemical potential ( $\tilde{\mu}_{H^+}$ ) is equal at all points of the system and so should be the potential of the pH electrodes. But many experiments show that the potentials of the pH electrode in the sediment and equilibrium solution of the same system are different, which allows the assumption that  $\tilde{\mu}_{H^+}$  is different from the equilibrium  $\tilde{\mu}_{H^+}$  at least at the indicator electrode.

The analyses of numerous experiments<sup>14,28,30,31</sup> suggests the assumption that the  $\tilde{\mu}_{H^+}$  change at the pH electrode is the consequence of the overlapping of the electrode double layer and those of the particles, at the point of intensive contact. This conception is in accordance with the statement that "as the double layers (of two charged surfaces!) overlap and get "compressed", the local ionic equilibrium at the surface may change, and this will clearly have an impact on the potential distribution...".<sup>32</sup> Following the above-cited vision of blocked "counterion reservoirs" this means that the reservoirs open because of the overlapping of the double layers. Some counterions are set free and microregions occur on the electrode surface where the concentrations (or partly even the species of the counterions!) and electrochemical reactions differ from the previous ones, and the former "single" electrode becomes a "double" electrode. The previous equilibrium electrode potential changes into the nonequilibrium steady-state mixed potential. So it is a consequence of the simultaneous general occurrence of the same electrode reaction proceeding at two different ion concentrations at different places on

the electrode. The continuance of this situation is due to the (not investigated) slowing down of reequilibration.

The surfaces of indicator electrodes (e.g. of glass-, antimony-, or bismuth- electrodes) may be very different,<sup>14</sup> so their mixed potentials are also different and variable in the same system, especially in a nonheterogeneous suspension.

The primary equilibrium is destroyed only in the proximity of particle contacts with the electrode surface, when these contacts occur. The rest of the system remains in equilibrium.<sup>3,cit 86</sup> The potential change of the indicator electrode in suspensions due to the influence of particles was termed the SE I (PWSE), as presented above. It must be measured by voltmeters having very high input resistance, otherwise the effects decrease or disappear.

### **Operational definition and interpretation of the SE**

Keeping in mind the original SE definition and taking into account all the argued statements of experimental and theoretical investigations in the prolonged study of the SE, one can accept the following operational SE definition and its interpretation,<sup>31</sup> based on this.

#### *Operational definition of the Suspension Effect*

The operational definition of the SE is equal to the early commonly accepted definition of the SE and means the difference of cell potential of a (suspension) galvanic cell for pIon measurement between the value obtained in a common procedure, with both electrodes of the cell in the suspension sediment and that when they are in its equilibrium solution.

#### *Interpretation of the Suspension Effect*

The SE is the algebraic sum of two effects; the SE I (PWSE) arises on the solid indicator electrode, the SE II (OSE) in the vicinity of the tip of the reference electrode salt bridge, when the electrodes are inserted in a suspension.

The cause of SE I is the interaction of the double layer of the indicator electrode with the double layers of particles when they are in close contact with it, resulting in a temporary, irreversible (steady state) mixed potential of the electrode. This potential can

be regarded as inherent to the SE and cannot be eliminated from cell potential measurements.

The cause of the SE II is the outflow or diffusion of solution from the tip of the reference electrode salt bridge into the suspension. Within the limits to which this solution diffuses among the suspension particles, an “anomalous liquid junction potential” arises. It is a systematic error and can be avoided in cell potential measurements.

It follows from this interpretation of the SE that in potentiometric measurements in suspensions both kinds of SE are consequences of irreversible electrochemical processes and therefore it is not possible to obtain directly exact thermodynamically founded  $p_{\text{Ion}}$  values from nonequilibrium cell potentials of suspension galvanic cells.

### **Consensus about the SE**

The question is appropriate; why for seventy years could a consensus about the SE not be attained, in spite of intense efforts of numerous investigators?

The objection to the first (Pallmann - Wiegner's) interpretation already included the fatal presumption that the electrode process on the indicator electrode is also reversible in suspensions. Because the potentiometric determination of ion activities (e.g. pH) is based on the Nernst equation, which is valid for equilibrium systems and was also applied in suspension galvanic cells, the presumably reversible electrode process on the indicator electrode was not questionable at all and it remained taboo for some up to this day.

In the same way Nikolsky's SE explanation, which in 1934 replaced that proposed by Pallmann, hindered (and still hinders today) a consensus about SE, in so far as it equalised the SE with the Donnan potential, which was later exchanged with the Donnan emf. As explained in the above discussion, all SE interpretations including the Donnan potential or the boundary potential difference of the sediment/equilibrium solution interface are unfounded and not valid, because this interface does not appear in either of the two galvanic cells which define the SE.

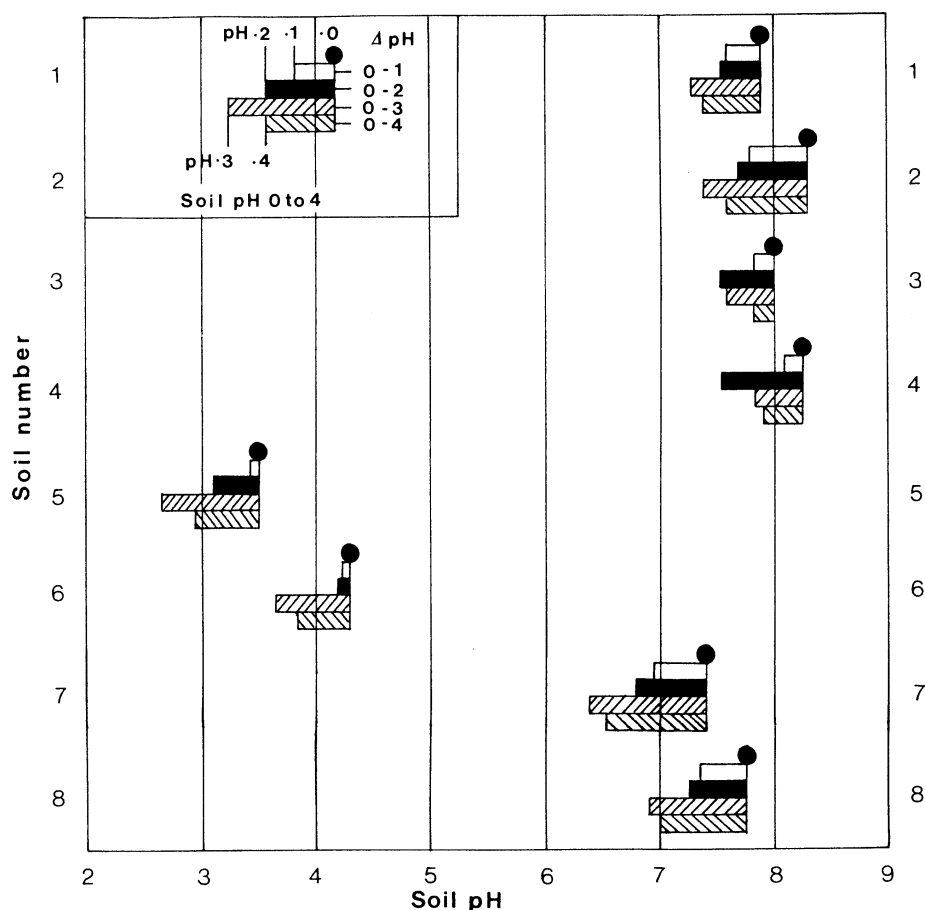
Almost all later attempts to explain the SE included or took in account one of the above hindering presumptions, which prevented the solution of the SE problem.

Is it now too much to expect, that seventy years after receiving its name, the SE will obtain its identity too?

*“Soil pH” in view of the above SE concept*

As it begun, this review should also finish with the problems of “soil pH” measurement. The different methods used nowadays<sup>33</sup> should be evaluated from the point of view of the above SE discussions. Fig. 1 may serve as the starting-point.

The pH values of eight wetted natural soils, chosen at random, which have different compositions and provenance, are given in Fig.1. As the most reliable soil pH value, the (operational) pH of the equilibrium solution of each soil is given first, and in relation to this the pH differences obtained with four other methods are presented.



**Figure 1.** “Soil pH values of wetted soils measured with five (pH 0 to 4) different methods, using the glass electrode and SCE. The differences  $\Delta\text{pH}$  between pH-0 (●) and other pH values (see text and inset) are given for comparison. The inset shows the legend of the symbols.

“Soil pH-0” is the pH value of the clear equilibrium solution, which was separated from the wet soil. The pH was measured in the usual way. The value obtained is equivalent to the pH of any clear solution measured in the same way. Because the equilibrium solution is in equilibrium with the wet soil,  $\tilde{\mu}_{H^+}$  is the same in both. But this does not mean that pH values are the same at all points of the soil, corresponding to Donnan partitioning, as mentioned above.

“Soil pH-1” is measured in the same wet soil sample, but prepared as a *combined suspension system*, the glass electrode being immersed in the soil and the tip of the reference electrode in the equilibrium solution. The difference (pH-1 - pH-0) represents the SE I, occurring due to the "liberation" of counterions during the interaction of particles with the indicator electrode. If pH-1 < pH-0, it can be assumed that most of the counterions around the particles are hydrogen ions.

“Soil pH-2” is the pH value obtained when both electrodes are inserted directly in the wet soil. Besides SE I, also the systematic error (pH-2 - pH-1) or SE II is included in the resulting pH reading, which differs from the "soil pH-0" by the value of the SE.

“Soil pH-3” is measured in the stirred suspension (or in its equilibrium solution) 24 hours after mixing the soil with KCl (0.1 M/l) solution. This can evoke different consequences (e.g. a change of the double layer structure or form, the "liberation" of some counterions from the particle double layers, followed by ion exchange, or chemical reactions with the solution), the result of which may be a considerable change of the pH value.

“Soil pH-4” is obtained by the same method as pH-3 except CaCl<sub>2</sub> (0.01 M/l) solution is used.

With the aid of the methods described it is possible to obtain for any soil five different pH values. The “soil pH-0” values and their differences from the pH values obtained with other four methods are various and specific for any soil, dependent on the soil characteristics. So it is possible to obtain from their comparison more information than any single pH value could give. It must be emphasized that pH values cited without specification of the method of measurement used are useless. On the other hand, the information obtained from comparison of the results obtained with the above mentioned

methods (probably not yet elaborated and evaluated enough) represents an argument that the “soil pH 0 to 4” values are useful in practical measurements, though a single “soil pH” may not be thermodynamically founded because of the “terrible” Suspension Effect.

Key words: Suspension Effect of the first and of the second kind; (Operational) definition of the Suspension Effect; Interpretation of the Suspension Effect; Mixed electrode potential in suspensions; Consensus about the origin of the SE; "Soil pH" estimations.

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### Povzetek

Podani so kratek, kritičen pregl ed študija suspenzijskega efekta (SE) od njegovega poimenovanja do danes, in vzroki, da ni bilo konsenza o njegovem izvoru in naravi.

Predstavljena je argumentirana (operacijska) definicija SE in na njej osnovana razlaga, da je SE vsota dveh efektov: prvega kot pojava ireverzibilnega mešanega potenciala indikatorske elektrode in drugega kot izjemnega tekočinskega potenciala ob stiku el ektrol itskega kl juča referenčne el ektrode s suspenzijo. V sistemih, v katerih nastopa SE, ionske aktivnosti niso natančno določljive, vendar je njihova ocena lahko koristna, kot je pokazano z določitvami "pH zemlje".