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Chemistry. — "Economic lixiviation." By Dr. P. J. H. v. GINNEKEN. (Communicated by Prof. ERNST COHEN.)

(Communicated in the meeting of June 28, 1913).

An economic lixiviation requires the attainment of a sufficient degree of leaching with as little solvent as possible, with the simplest contrivances and in the shortest possible time.

Let us take a mass R + Saq, consisting of a substance R insoluble in water¹) and of a watery solution of the water-soluble substance S. A definite quantity of this mass has to be lixiviated with water in the most economical manner.

We assume that the solution is combined with the solid substance capillarily, by absorption, by inclusion in permeable walls or by other means, but not chemically; and also that during the lixiviation the volume of the liquid combined with the solid substances in this manner does not change.

We equal this volume of the "combined liquid" in a definite weight of the original mass to v.

By V we represent: the volume of the water (or of the solution respectively) which is added to a definite weight of the original mass in each period of the lixiviation. In the following considerations we assume that this volume also does not change during the lixiviation by absorption of the substance S. The solution obtained after each period has, therefore, also the volume V. This assumption will (like that about v) be only roughly approximate in the case of larger concentrations; in each case, therefore, we shall have to account for the extent of the deviation and of the influence thereof on the results obtained. We put V = v

on the results obtained. We put $\frac{V}{v} = x$.

By b_0 is represented the concentration²) (expressed in grams per 100 cc.) of the substance S in the combined liquid of the original mass, by $b_1, b_2, \ldots b_n$ the corresponding concentrations during or after the lixiviation, respectively:

By $U = \frac{b_0}{b_n}$: the degree of lixiviation indicating how many times

the concentration in the combined liquid has been reduced owing to the lixiviation;

by a_{σ} : the concentration of the solution resulting from the whole process;

¹⁾ All this applies mutatis mutandis to an arbitrary solvent.

²⁾ Unless stated otherwise, the concentration will in future mean gram per cc

by $a_1 a_2 \ldots a_{n-1}$: the concentrations of the solutions obtained in the different periods of lixiviation.

BUNSEN¹) has shown that on washing a precipitate with water there is obtained, after n washings with a volume V, the degree of lixiviation:

wherein W = nV indicates the total volume of the added water.

He further shows that the amount of water required to attain a definite degree of lixiviation gets smaller and nears a value limit when the water is added each time in smaller quantities. As value limit for U we find:

If now we wish to go further and try to obtain a larger degree of lixiviation, we shall have to divide the mass itself into smaller portions and apply the counter-current principle. BUNSEN, in his calculation, assumes that on each addition of water, the combined liquid and the water added are mixed homogeneously. In practice, this is mostly not the case We will, however, provisionally adhere to this assumption in order to deduce a few general *data*.

Discontinuous lixiviation, according to the counter-current principle, at a very great lixiviation velocity or a very long period of lixiviation.

Let us suppose that the process is working in the usual manner. In each period of the lixiviation, mixing takes place of definite quantities of the mass (with volumes of liquid v) with a definite volume of solution (or water, respectively) V, after which follows filtration.

Let us place the concentrations of the quantities underneath each other in the following manner:

After the lixiviation has taken place and filtration has been resorted to, the concentrations of the residual lixiviated quantities and of the appertaining filtrates may then be represented by

¹) Lieb. Ann 148, 269 (1868). The quantity v has been defined by BUNSEN slightly differently to that given above.

A displacement of the symbols b each a place to the right and of the symbols a each a place to the left reestablishes the first condition.

For the first element of the series we can now write the equation $vb_0 + Va_1 = vb_1 + Va_0$

or

and further:

If now we suppose that we are waiting first for a complete setting in of the equilibrium before filtering, it follows that $a_0 = b_1$, $a_1 = b_2$ etc. so that the above equation becomes:

$$b_{0} + xb_{2} \equiv (1+x) b_{1}$$

$$b_{1} + xb_{3} \equiv (1+x) b_{2}$$

$$\vdots$$

$$b_{n-2} + xb_{n} \equiv (1+x) b_{n-2}$$

$$b_{n-1} \equiv (1+x) b_{n}$$

From these *n* equations we can eliminate $b_1, b_2 \dots b_{n-1}$ after which there remains a relation between b_0 , b_n and *x* which may be written

$$\frac{b_0}{b_n} = U = 1 + x + x^2 + \ldots + x^n = \frac{x^{n+1} - 1}{x - 1} \cdot \ldots \cdot (A)$$

From this expression for U can be deduced:

If n is constant, U increases indefinitely with x.

If x is constant and >1: U increases indefinitely with n.

If x is constant and < 1: U increases with n, but is maximal $\frac{1}{1-x}$. If U is kept constant, x decreases with increase of n, but is minimally equal to $1 - \frac{1}{U}$.

Hence, in the most favourable conditions there must be added, in order to lixiviate a mass with a volume of liquid v to a degree of lixiviation U, a volume of water $\geq \frac{b_0 - b_n}{b_0} v$.

As a rule the expression found for U cannot, however, be applied to the methods of leaching used in practice.

If we mix a mass, which in some non-chemical manner holds a liquid in combination, with a more diluted solution, these solutions will not mix immediately, because as a rule the same force that causes the combination of the first liquid will oppose the immediate mixing. As long as no perfect equilibrium has set in, two layers will continue to exist and the formation of the equilibrium will take place, the solid substance S diffusing from the more concentrated layer into the other one.

In this sense each lixiviation process is a diffusion process.

We assume that the quantity of weight of the substance S, which in a short time unit dt, diffuses from the volume v into the volume V can be represented in the following manner:

wherein K represents the quantity of the substance S which diffuses in the time unit per unit of surface and per unit of (constant) concentration difference; O represents the surface of the dividing layer between the two volumes of liquid, b - a represents the (during the time dt, constant) difference in concentration²).

We now distinguish the following three cases :

I. Discontinuous lixiviation according to the counter-current principle with a limited number of volumes which, in regard to the concentration are homogeneous.

II. Semi-continuous lixiviation 'according to the counter-current principle with a limited number of volumes which, with regard to the concentration are homogeneous.

III. Continuous lixiviation according to the counter-current principle with a very large number of layers homogeneous with regard to the concentration.

1. Discontinuous lixiviation according to the counter-current principle.

We have already detailed above this method of working p. 202). Only, this time the filtration is not postponed until the equilibrium has set in.

Let us consider the changes in concentration in one element during the finite period of lixiviation.

In the first element we have before the diffusion the concentrations b_0 and a_1 , afterwards b_1 and a_0 . This again gives rise to the equation:

We can now find another relation between the same quantities if we ascertain how the initial and final condition are converted into each other during the diffusion time Δt .

The amount of the substance S which in a small unit of time dt passes from the one layer into the other, may be expressed in three ways:

¹) Cf. note 2 p. 201.

 $ds = KO (b-a)dt = -vdb = Vda \quad . \quad . \quad . \quad . \quad (5)$ From the two last terms of this equality follows:

$$da = -\frac{1}{\sqrt{n}} \, db.$$

Integration of the two members of this equation over the time t = 0 up to t = t' when $0 < t' < \Delta t$ and $b_{t=0} = b_0$ and $a_{t=0} = a_1$ gives the equation

$$a-a_1=-\frac{1}{x}(b-b_0),$$

from which follows

$$b-a = \frac{x+1}{x} b-p,$$

wherein

$$p = a_1 + \frac{1}{x} b_0.$$

If in the second term of the equality (5) we substitute this value for b-a, we obtain from the second and third term, after rearrangement, the equation:

$$\frac{db}{b - \frac{x}{x+1}p} = -\frac{KO}{v} \cdot \frac{x+1}{x} dt$$

in which $\frac{KO}{v} \cdot \frac{x+1}{x}$ is independent of the time.

Integration yields:

$$b - \frac{x}{x+1}p = e^C \times e^{-\frac{KO}{v} - \frac{x+1}{x}t}$$

If now we remember that $b_{t=0} = b_0$, it follows that

$$b - \frac{x}{x+1} p = \left(b_{\circ} - \frac{x}{x-1}p\right) e^{-\frac{KO}{v} \cdot \frac{x+1}{u}t}$$

If now we substitute for $t, \Delta t$ and for b the corresponding value b_1 and if also we again replace p by $a_1 + \frac{1}{x} b_0$, we obtain after rearrangement having regard to (3)

$$b_{0} - a_{1} = (b_{1} - a_{0}) e^{\frac{1}{v} \cdot \frac{1}{x} \Delta t} \cdot \dots \cdot (6)$$

Hence, for each element of the lixiviation battery, we have two equations (3 and 6). If the battery contains n elements we may put $\Delta t = \frac{t_n}{n}$ when t_n represents the total period of lixiviation of a quantity of the mass.

Hence, we find together the following $2 \times n$ equations:

$$\begin{array}{c} b_{0} + xa_{1} = b_{1} + xa_{0} \\ \vdots \\ b_{n-2} + xa_{n-1} = b_{n-1} + xa_{n-2} \\ b_{n-1} = b_{n} + xa_{n-1} \end{array} \right) \begin{array}{c} b_{0} -a_{1} = (b_{1} - a_{0}) K' \\ \vdots \\ b_{n-2} - \sigma_{n-1} = (b_{n-1} - a_{n-2}) K' \\ b_{n-1} = (b_{n} - a_{n-1}) K' \end{array} \right)$$
(6)

If from this we eliminate $a_0, a_1, a_2, \ldots, a_{n-1}$ there remain *n* equations, which may be written in this manner

in which

$$q = K'x + 1 = xe^{\frac{KO}{v}} \cdot \frac{x+1}{x} - \frac{t_n}{n} + 1$$
$$p = K' + x = e^{\frac{KO}{v}} \cdot \frac{x+1}{x} - \frac{t_n}{n} + x$$

Elimination of the n-1 values $b_1 \ldots b_{n-1}$ gives, after rearrangement, the relation

If we add together the equations (3) then

Hence, if b_0 is known and b_n obtained from (I) a_0 may be calculated from (8) also.

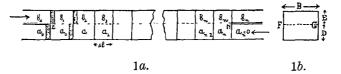
If KO (or t_n) is very large we get $\frac{q}{p} = x$ so that we find for U the expression that we have deduced previously for very great diffusion velocity (or a prolonged period of leaching).

The discussion of the expression found will be found below in connexion with the results of the other working processes.

A lixiviation process which is being conducted in a continuous manner may be brought in the following manner in a form, which renders possible a mathematical formulation 1).

¹) See note 1 p. 209.

The space of which fig. 1a represents the longitudinal and fig. 1b the cross section is divided into two parts by a plane LN (or FG,



respectively). In the upper space the mass to be lixiviated moves from the left to the right (we call this direction positive) in the lower space the lixiviating liquid moves in the opposite direction. The wall LN (or FG, respectively) which separates the two liquid layers corresponds in reality either with a boundary layer between two layers of liquid or with an actually existing permeable wall. The dimensions of the whole have been chosen in such a manner that the size of the surface LNFG is equal to the surface of the actual dividing layer between the two volumes of liquid, and also that the volumes of the upper and lower space are in the proportion of v: V. (Hence, the volume of the insoluble matter R present in the mass has not been taken into consideration). From this arrangement, it follows that the velocity of motion of the mass to be lixiviated and that of the lixiviating liquid are equal ¹).

II. Semi-continuous lixiviation according to the counter-current principle.

Let us imagine, as indicated in fig. 1*a*, the whole space to be divided, by planes perpendicularly to the longitudinal direction, into a finite number (n) of equal parts whose length is Δl .

In each of the thus formed divisions the liquid is homogeneous in regard to the concentration. A small quantity of liquid which flows from one division into another will at once mix homogeneously with the liquid contained therein. The condition in the whole system is stationary; hence, the concentration in each division is constant and is indicated by the letters inscribed.

Let us imagine the process to be in operation. The mass is moved along with a velocity $\frac{dl}{dt}$, the lixiviating liquid has the velocity $-\frac{dl}{dt}$. Let us consider the divisions in which the concentration is b_1 or a_0 , respectively.

The amounts (*ds*) of the substance S which, in the small period of 3) See note 1 p. 210. time dt, passes through the dividing wall from $[b_1]^1$ into $[a_0]$ can be again expressed in three ways. As b_1 is constant, ds must also be equal to the difference of the quantities of the substance S, which enter and leave in the time $dt \lfloor b_1 \rfloor$; the same applies to $[a_0]$.

In this way we find:

$$ds = KB \bigtriangleup l (b_1 - a_0) dt = BE \frac{dl}{dt} dt (b_0 - b_1) = BD \frac{dl}{dt} dt (a_0 - a_1) \quad (9)$$

If we put $\frac{dl}{dt} = \frac{n\Delta l}{t_n}$ in which t_n represents the total period of

lixiviation of the mass and if we consider that $\frac{D}{E} = \frac{V}{x} = x$ and that

we can write $\frac{K \cdot B \cdot \Delta l}{EB\Delta l} = \frac{KO}{v}$ it follows that

$$\frac{KO}{v}(b_1-a_0) = (b_0-b_1)\frac{n}{t_n} = x(a_0-a_1)\frac{n}{t_n} \quad . \quad . \quad (10)$$

In the same manner may be deduced 2(n-1) other equations (10), which relate to the other divisions.

In an analogous manner as in the discontinuous lixiviation we find from these equations:

$$\frac{b_0}{b_n} = U = \frac{x\left(\frac{q}{p}\right)^n - 1}{x - 1} \dots \dots \dots \dots (II)$$

in which

$$q = \frac{KO}{v} + \frac{n}{t_n}$$
$$p = \frac{1}{v} \frac{KO}{v} + \frac{n}{t_n}$$

This expression shows, therefore, a similarity to that of the discontinuous lixiviation. q and p, however, have a quite different value.

From the equations (10) may be again deduced by addition

 $b_0 - b_n \equiv x a_0, \quad \dots \quad \dots \quad \dots \quad (8)$

- • .

by which a_0 is expressed in b_0 and b_n (or U, respectively.)

From the equations (10) may be deduced also a universal expression for the concentrations b.

This expression has the form:

1) By $[b_1]$ is meant the division containing the concentration b_1 .

$$\frac{b_y}{b_n} = \frac{x\left(\frac{q}{p}\right)^{n-y} - 1}{x - 1}$$

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in which y indicates the figure that is written as index at the concentrations b. With the aid of this equation it is possible to draw a figure which indicates the progressive change of the concentrations b at the semi-continuous lixiviation.

III. Continuous lixiviation according to the counter-current principle.

We pass from the semi continuous lixiviation to the continuous one by taking n very large and Δl very small.

In the same manner as in the continuous lixiviation we find here $: ^{1}$)

$$ds = KB \Delta l_b (b_1 - a_0) dt = BE \frac{dl}{dt_b} dt (b_0 - b_1) = -BD \frac{dl}{dt_a} dt (a_0 - a_1) . (12)$$

in which

in which

$$\frac{dl}{dt_b} = -\frac{dl}{dt_a}$$
 and $\Delta l_b = -\Delta l_a$.

If now we replace generally $b_1 - a_0$ by b - a, (b and a being variable quantities dependent on l) and write:

$$b_0 - b_1 = -\frac{db}{dl} \Delta l_b$$

and

$$a_{\mathfrak{o}} - a_{\mathfrak{i}} = \frac{da}{dl} \, \Delta l_a$$

and if we substitute

$$\frac{K}{E} = \frac{KO}{v}$$
; $\frac{K}{D} = \frac{KO}{V}$ and $\frac{D}{E} = v$

we get:

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1) A deduction which agrees in principle with the one made here is given by VAN LOON (Tijdschrift der Algemeene Technische Vereeniging v. B. en R. 1911-1912 p. 231). In my opinion, however, the method used is not quite correct. This does not prevent, however, that in the article cited there are mentioned many very correct and original remarks on this subject.

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The latter equation yields by integration of the two terms

$$a = \frac{1}{x}b + const.,$$

from which follows, because when a = 0, $b = b_n$

0r

$$b-a = \frac{x-1}{x}b + \frac{1}{x}b_n.$$

Substitution of this value for b-a in (13) and rearrangement gives

$$\frac{db}{b+\frac{1}{x-1}b_n} = -\frac{1}{s_b} \cdot \frac{KO}{v} \cdot \frac{x-1}{x} dl$$

in which

$$s_b = \frac{dl}{dt_b}$$

Integration yields:

$$b + \frac{1}{x-1} b_n = e^{const} \times e^{-\frac{KO}{v} \cdot \frac{x-1}{x} \cdot \frac{l}{s_b}}$$

from which follows, because when l = 0, $b = b_0$:

$$b + \frac{1}{x-1}b_n = \left(b_0 + \frac{1}{x-1}b_n\right)e^{-\frac{KO}{v}\cdot\frac{x-1}{2}\cdot\frac{l}{s_b}} . . . (16)$$

This equation is that of the line which represents the progressive change of the concentration b as a function of l. If we want to represent b as a function of the time, we can substitute $\frac{t}{s_i} = t$.

By performance of this last substitution and substitution for band t of the corresponding values b_n and t_n and some rearrangement. we now find from (16) the expression 1 for U:

¹⁾ The expression found also applies to the case when the volumes of the two spaces in which move the combined liquid and the lixiviating liquid do not stand in the proportion of $\frac{v}{V}$. In that case $\frac{dl}{dt_b}$ is not equal to $-\frac{dl}{dt_a}$ and t_n not equal to t_{n_b} . The deduction is made in the same manner, when $\frac{D}{E} \frac{dl}{dt_a} = \frac{V}{v} = x$. We obtain for *U* the average

We obtain for U the expression (III) but must therein replace t_n by t_{n_b} . Hence (with equal x) it is a matter of indifference for the leaching whether the

$$\frac{b_{\mathfrak{o}}}{b_n} = U = \frac{\frac{KO}{v} \cdot \frac{x-1}{x} t_n}{x-1} \dots \dots \dots (III)$$

in which for t_n may also be written $\frac{t_n}{s_b}$ (l_n = total length).

It is possible to deduce this expression for U (continuous) straightway from the expression for U (semi-continuous) and also from that for U (discontinuous) by rearranging these expressions in a suitable manner and putting $n = \infty$.

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From (15) and (16' we find the equation ') which indicates the relation between the concentrations a and the length l (or the duration t):

$$a + \frac{1}{x - 1} b_n = \frac{1}{x} \left(b_0 + \frac{1}{x - 1} b_n \right) e^{-\frac{KO}{v} \cdot \frac{x - 1}{x} \frac{l}{s_b}} \dots \dots (17)$$

From (15) again follows:

from which a_0 can again be calculated if b_0 , U, and x are known.

The relations deduced above furnish a means for calculating for each method of working the results obtainable (U or b_n ; and a_o if the quantities K, O, v, V, t_n $\left(l_n$ and $\frac{dl}{dt}$, respectively) and n are known or can be determined.

K and O. As the quantity K (the choice of the units being determined) accounts for all the specific properties of the mass to be leached, it will as a rule have to be determined experimentally. Up to now we have assumed silently that K has no connexion with O, but this supposition will, in many cases, not be correct. In the lixiviation of masses where the bound liquid is not found at the surface of the solid substance, but must proceed a certain distance dependent on the thickness of the solid particles, K will, as a rule, change with O²). As, however, as a rule O will also not be capable of direct measurement, the product of the two quantities will, in such cases, have to be introduced as a single constant. Of course, the nature of the substance must be such that this quantity remains really constant during the whole process.

space at disposal for the lixiviating liquid is taken larger or smaller. In practice the_opinion is often met with that such an influence is really present.

¹) We may, of course, deduce this equation also from (14) and (15) in the same manner as (16) was deduced from (13) and (15).

²) Cf. van Loon l.c.

v, for instance can be found from the amount of solid substance R contained in the mass and the sp. gr. of the bound liquid.

In most cases v will occur in the formula as a *quantity* specific and constant for the material. If, however, the lixiviation is assisted by pressing so that during, or after each filtration the "natural" volume v is reduced to v', v will be variable and the result of the lixiviation be dependent on the value of v'. Hence the formulae found show also the influence of the degree of pressing on the lixiviation.

I. Because, as we have assumed, this *quantity* remains constant during the process, V can be measured as the volume of water added, or as the volume of solution obtained. In how far the said assumption is correct or not and its eventual influence on the results, must be ascertained for each case.

 t_n , l_n and $\frac{dl}{dt}$ (continuous and semi-continuous). By varying these quantities (in which $t_n \frac{dl}{dt}$ always $= l_n$) we can ascertain the influence of changes in these quantities on the results of the lixiviation. It should be observed here that for a definite apparatus $\frac{dl}{dt}$ is proportional to the yield.

 t_n , n and Δt (discontinuous). Here $t \frac{1}{\Delta t} = n$ and $\frac{1}{\Delta t}$ is proportional to the yield.

n. When in the discontinuous and semicontinuous lixiviation n is taken very large these two methods of working change into the continuous method, which fact can, moreover, be readily demonstrated mathematically from the formulae found.

If for a definite case we calculate U_D (discontinuous) and U_S (semicontinuous) for different values of n we can ascertain, for both methods of working, what is the influence of the value of n on U. U_D and U_S then near the value limit $U_{n=\infty}$ or U_C (continuous). We have applied this calculation to the following values for KO, t, V and v and U_C , which values agree with a case met with in practice.

$$KO = 15,6$$

 $t = 75$ (minutes)
 $V = 105$ (cc. %/0 gr.)
 $v = 88$ (cc. %/0 gr.)
 $U_C = 48$

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The subjoined table gives the values found:

n	U _D	U _S
10	22.0	11.1
20	37.0	18.3
30	42.4	23.3
100	47.5	36.9
200	47.6	41.8
8	48	48

In fig. 2 are drawn the lines which have been constructed with these values. They run asymptotical in regard to the line U = 48.

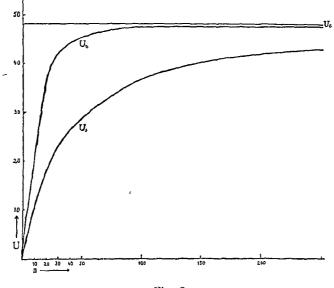


Fig. 2.

It is evident that, for a case as the one cited here, n being equal, the semi-continuous method gives much less favourable results than the discontinuous one.

Now, in some cases, however strange it may sound, it is not always easy to make out which method we are dealing with. For instance, "battery work" is by no means always discontinuous or even semicontinuous, but is often very much like the continuous method of working. When the succession of the concentration layers is not disturbed by mechanical motion or an unfavourable form of the space (dead space)¹), battery work is in many cases to be preferred to other methods of working. The fact that the apparatus which move along the mass to be leached and therefore cause apparently a perfect continuous process, often give results less favourable, is to a great extent due to the mechanical motion disturbing the succession of the concentration layers in the mass; owing to this the process becomes no longer continuous but changes into the most unfavourable semi-continuous form.

Finally, attention may be called to the following application of the matter considered. We have assumed that the liquid used for the lixiviation of the mass R + Sag consisted of pure water. If now we suppose that the lixiviating liquid was contaminated, before the leaching, with another dissolved substance Z, the question arises what influence this will exert on the products obtained.

We now readily perceive that in the lixiviation process the action of the two liquids on each other is quite mutual and that we can just as well "lixiviate" the lixiviating liquid with the combined liquid as doing the reverse. If the process is conducted in a rational manner this will benefit the one (real) as well as the other (secondary) lixiviation. The bulk of the impurity Z does not then arrive in the final liquid, but in the exhausted mass. To the secondary lixiviation we can apply *mutatis mutandis* the same formula which applies to the lixiviation proper.

When carrying this out it appears that when a larger V is taken, the result of the lixiviation proper improves whilst that of the secondary lixiviation gets worse. (Of course, the values of K are not the same).

This application also has significance in practice. For it has occurred that for the leaching water was used with considerable contamination, and yet the contamination of the liquid obtained proved rather small. Such a method of working will, however, always be attended with the difficulty that a slight disturbance in the continuity of the lixiviation (which disturbance would otherwise cause merely a dilution of the final liquid) will now cause a strong contamination of the resulting liquid.

The above study was carried out with a technical object. On the practical application of the results obtained a communication will be made in a trade journal.

May 1913.

¹) VAN LOON I.C.