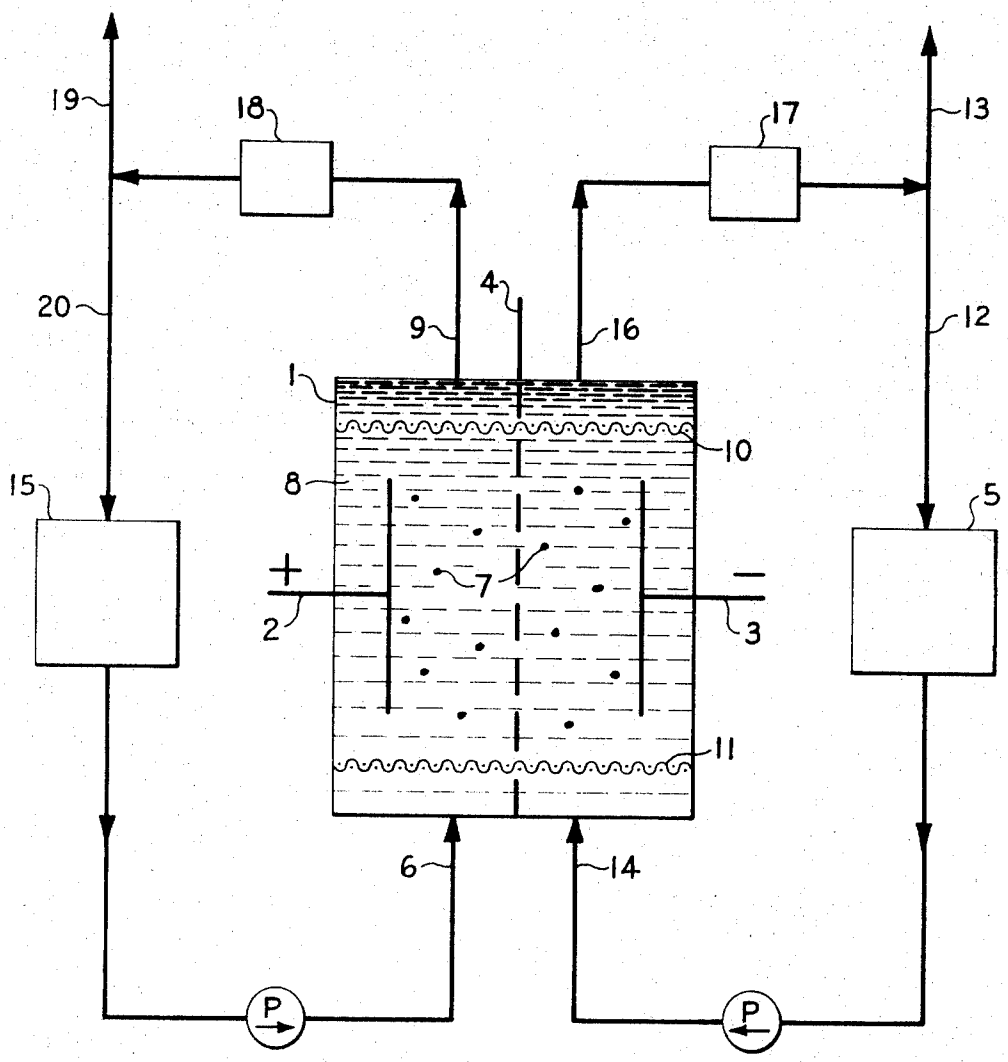
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DECREASING HEXAVALENT CHROMIUM CONTENT OF LIQUIDS BY AN ELECTROCHEMICAL TECHNIQUE

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DECREASING HEXAVALENT CHROMIUM CONTENT OF LIQUIDS BY AN ELECTROCHEMICAL TECHNIQUE

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ABSTRACT OF THE DISCLOSURE

A method for decreasing the hexavalent chromium content of a solution which comprises passing an electric current through a solution containing hexavalent chromium material, which solution is contained as the electrolyte in a cell, said cell having at least one positive and one negative electrode, between which the current is passed, and wherein the electrolyte also contains a bed of particles, distributed therein, such that the porosity of the bed is from about 40 to 80%, porosity being defined as

$$\left(1-\frac{\text{volume of particles}}{\text{volume of cell wherein the particles are distributed}}\right)\times 100$$

The electrolysis of the electrolyte is continued until the desired reduction in the hexavalent chromium content thereof is obtained.

This invention relates to a process for treating solutions which contain hexavalent chromium materials and more particularly it relates to an improved electrochemical process for decreasing the hexavalent chromium content of a solution.

In various industries, solutions are utilized which contain hexavalent chromium materials and the disposal of these, poses a significant pollution problem. For example, various hexavalent chromium compounds are frequently added to much of the cooling water used in various industrial processes, to inhibit corrosion and retard the growth of algae. Additionally, in the metal treating industry, hexavalent chromium plating baths, conversion coating solutions and rinses are widely employed. Although heretofore, various chemical techniques have been proposed for the treatment of such hexavalent chromium containing effluents, these have generally been either inefficient or too expensive or have resulted in the formation of products whose disposal presents as many pollution problems as the hexavalent chromium materials themselves. Accordingly, there has recently been a great deal of effort expended in the development of new and different processes for the treatment of these hexavalent chromium containing effluent solutions.

In Belgium Pat. 739,684, for example, there is described an electrochmeical technique wherein a semi-conductive bed of solid particles is used to oxidize various substances to non-toxic forms. Another process, utilizing an electrochemical technique is described in New Scientist June 26, 1969, page 706. In these and similar processes which have recently been proposed, the electrochemical systems utilized have been found to be both inefficient, and/or uneconomical and require frequent changing of the bed of particles which is utilized. Accordingly, these systems have not met with any appreciable commercial utilization.

It is, therefore, an object of the present invention to provide an improved process for treating solutions containing hexavalent chromium materials so as to reduce the hexavalent chromium content of such solutions.

A further object of the present invention is to provide an improved process for reducing the hexavalent chromium content of a solution by means of an efficient and economical electrochemical treatment.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows:

Pursuant to the above objects, the present invention includes a process for treating a solution containing hexavalent chromium materials to decrease the hexavalent chromium content thereof which comprises passing an electric current through the solution which contains the hexavalent chromium materials, which solution is contained as the electrolyte in a cell, said cell having at least one positive and one negative electrode, between which the current is passed, and wherein the electrolyte also contains a bed of particles, distributed therein such that the porosity of the bed is from about 40 to 80%, porosity being defined as

$$\left(1-\frac{\text{volume of particles}}{\text{volume of cell wherein the particles are distributed}}\right)\times 100$$

By carrying out the electrochemical treatment of the solutions containing hexavalent chromium materials in this manner, it has been found to be possible to reduce the concentrations of these materials in the solutions from the parts per million level to the parts per billion level.

More specifically, in the practice of the method of the present invention, the solutions which are electrolyzed to effect the reduction in the hexavalent chromium content thereof, i.e., the electrolyte solutions in the cell, may be various solutions which contain hexavalent chromium materials although, preferably, these are aqueous solutions. These solutions may contain varying amounts of the hexavalent chromium materials, solutions containing as much as 10% by weight and as little as one part per million of hexavalent chromium being suitable for treatment in accordance with the process of the present invention to effect a reduction of the hexavalent chromium content. In referring to the hexavalent chromium materials in the solutions, it is intended to include the various compounds in which the chromium is present in the +6 valence state, such as chromates, dichromates, chromic oxide, chromic acid, and the like. Additionally, it is intended to include various organic-chromium compounds, as well as the inorganics.

The solutions containing hexavalent chromium materials which are to be treated in accordance with the present method may come from various sources. Thus, for example, as has been indicated hereinabove, they may be effluent streams from chromium plating processes, chromate conversion coating solutions and chromate rinse solutions from metal treating process, as well as cooling water from industrial plants which contains hexavalent chromium materials. The method of the present invention may be used not only to reduce the content of hexavalent chromium materials in industrial and similar waste streams, but, additionally, may also be used to effect substantially complete removal of relatively small amounts of hexavaent chromium materials, as a final purification step in the treatment of water intended for human consumption. The solutions treated may also contain various other components, in addition to the hexavalent chromium materials, and may include mixed effluent streams from several different industrial processes. Thus, for example, the solutions may contain in addition to the hexavalent chromium materials, sulfates. fluorides, silicofluorides, trivalent chromium, phosphates, and the like, as are present in typical plating and coating baths, as well as chlorine, HCl, hypochlorites, hypochlorous acid, and the

like. Such solutions are, however, merely exemplary of the effluent solutions which may be treated.

The pH of the solution to be treated may vary over a wide range, being either acidic, neutral or basic, pH values of from about 1 to 14 having been found to be suitable. Desirably, the pH is from about 5 to 10 with a pH range of from about 6 to 9 being particularly preferred. Depending upon the makeup of the solution which is to be treated, adjustment of the pH may be done by the addition of various "support" electrolytes to the hexavalent chromium containing solution. Suitable "support" electrolytes which may be used are aqueous solutions of borates, ammonia, sodium chloride, sulfuric acid, calcium chloride, sodium cyanide, chloroacetates, sodium hydroxide, sodium bicarbonate, hydrochloric acid, and the like.

The temperature of the electrolyte, i.e., the solution being treated, may also vary over a wide range, the only criteria being that at the temperature used, the electrolyte remain a liquid. Thus, temperatures within the range of about 0 to 100 degrees Centigrade have been found, generally, to be suitable. For economy in operation, however, it has frequently been found to be preferred to utilize these solutions at ambient temperatures. Similarly, the present process is desirably carried out at atmospheric pressure although either sub- or super-atmospheric pressures may be employed, if desired. It has been found in some instances, however, that the use of elevated temperatures, e.g., 60–70° C., may be desirable in effecting a more rapid reduction in the hexavalent chromium content, depending upon the particular "support" electrolyte, pH range, type and concentration of hexavalent chromium which are used.

As has been noted hereinabove, the electrolyte, i.e., the solution being treated, is contained, during treatment, in a suitable electrolytic cell and contains a bed of particles which are distributed in the electrolyte in the cell, such that the porosity of the bed ranges from about 40 to 80%, porosity being defined as:

$$\left(1-\frac{\text{volume of particles}}{\text{volume of cell wherein the particles are distributed}}\right)\times 100$$

By determining the density of the particles used and weighing them, the term "volume of the particles" in the above porosity formula may be replaced by the value for the weight of the particles divided by the true density of the particles. The particle density can be measured by filling a one liter container with particles, the weight of which is known. Then, an electrolyte is added to the container to fill the voids between the particles, the amount of electrolyte needed being measured as it is added. The true density of the particles, in grams per $cm.^3$, is the weight of the particles in grams divided by the true volume of the particles in $cm.^3$. The true volume of the particles is the bulk volume minus the volume of the voids in the particle bed, the latter being the volume of the electrolyte which is added to the one liter container. Thus, the true volume of the particles in this instance would be 1000 cubic centimeters minus the volume of the voids, i.e., the volume of electrolyte added to the container.

It will, of course, be apparent that the porosity of the bed of particles maintained in the electrolyte which is being treated in the cell may be varied and that with different types of particles, under the same operating conditions or with similar particles under different operating conditions, changes in the bed porosity will take place. Thus, the true density of the particle will vary depending upon the porosity of the particles themselves, e.g., graphite as compared to glass beads, with similar variations in density being effected by the electrolyte itself because of the differences in the surface tension of various electrolyte solutions. Additionally, since the particles of the bed are generally dispersed or distributed by the flow of the electrolyte through the cell, variations in the flow characteristics will also result in changes in the bed porosity.

To illustrate this latter situation, if a one liter container were filled with particles of a particular size and shape, using the formula given above, the porosity of this bed of particles would be:

$$1-\frac{\text{volume of particles in cc.}}{1000\text{ cc.}}\times 100$$

If the same quantity of particles were then distributed by the flow of the electrolyte, such that the volume of the bed now reached two liters, using this same formula, the porosity of the bed is now

$$1-\frac{\text{volume of particles in cc.}}{2000\text{ cc.}}\times 100$$

Clearly, in the second instance, the porosity of the bed has increased. As has been noted above, the porosity of the bed of particles dispersed in the electrolyte may range from about 40 to 80%. In many instances, a preferred range for the bed porosity is from about 55 to 75% with a specifically preferred range being from about 60% to 70%.

The particles employed to form the porous bed in the present process typically are solid, particulate materials that may be conductive, non-conductive or semi-conductive. By "conductive" it is meant that the material of which the particles are made will normally be considered on electron-conducting material. Where the particles are conductive, they may have a metallic surface, either by virtue of the particles themselves being metallic or by being made of non-conductive material on which a metallic surface has been deposited. Typical of the metals which may be employed are the metals of Group VIII of the Periodic Table, such as ruthenium and platinum, as well as other conductive elements, such as graphite, copper, silver, zinc, and the like. Additionally, the conductive particles may be electrically conductive metal compounds, such as ferrophosphorus, the carbides, borides or nitrides of various metals such as tantalum, titanium, and zirconium, or they may be various electrically conductive metal oxides, such as lead dioxide, ruthenium dioxide, and the like. Where the particles are non-conductive, they may be made of various materials, such as glass, Teflon® coated glass, polystyrene spheres, sand, various plastic spheres and chips, and the like. Exemplary of various semi-conductive materials of which the particles may be made are fly ash, oxidized ferrophos, zirconia, alumina, conductive glasses, and the like.

The particles used desirably range in size from about 5 to 5000 microns, with particle sizes of from about 50 to 2000 microns being preferred. In many instances a particularly preferred range of particle sizes has been found to be from about 100 to 800 microns. Although it is not essential to the successful operation of the process of the present invention that all of the particles in the porous bed distributed in the electrolyte have the same size, for the most preferred operation of the process, it has been found to be desirable if the range of particle sizes is maintained as small as is practical.

It has further been found that the density of the particles used should be such, that in conjunction with the size and shape of the particles, it will provide the proper balance between the drag force created by the electrolyte motion and the buoyancy and gravitational forces required to achieve particle dispersion or distribution at the desired bed porosity. Thus, where the particle dispersion is established against or in opposition to the buoyancy force, the particle densities typically may range from aboutt 0.1 (less than the density of the electrolyte) to about 1.0 grams per cc. Where the particle dispersion is achieved against or in opposition to the gravitational force, the particle densities typically may range from about 1.1 to 10 grams per cc. and preferably from about

1.5 to 3.5 grams per cc. The most preferred operating conditions have been found to be when the particles are dispersed throughout the electrolyte, within the cell, during the movement of the electrolyte and when the particles are more dense than the electrolyte.

The electrolytic cell may be of any suitable material and configuration which will permit electrolysis of the hexavalent chromium containing solution to effect a reduction in its hexavalent chromium content and which will permit retention of the porous bed of particles in the electrolyte, within the cell. Exemplary of suitable materials of construction which may be used for the cell are various plastics, such as the polyacrylates, polymethacrylates, polytetrahaloethylenes, polypropylenes, and the like, rubber, as well as materials conventionally used in the construction of chlor-alkali cells such as concretes. Additionally, the cells may be made of metal, such as iron or steel. In such instances, electrically insulating coatings should be provided on the metal surfaces in the cell interior or electrical insulation provided between the metal of the cell and the electrodes.

The size of the electrolytic cell may also vary widely, depending upon the nature and quantity of the hexavalent chromium containing solution which is to be treated. Thus, where appreciable quantities are involved, as in the treatment of industrial wastes or as a part of a water purification system, the cell may be relatively large and include a multiplicity of treating zones, whereas for the treatment of water for individual home use, appreciably smaller units may be utilized, similar in size to conventional "soft-water" treating units. Additionally, the cell may be of a suitable size so as to be portable, for use at camp sites, and the like. Typically, the cell will have a suitable inlet and outlet means for introducing and removing the solution to be treated, means for retaining the porous bed of particles dispersed in the electrolyte within the cell, means for supporting at least one positive and one negative electrode in contact with the electrolyte in which the porous bed of particles is distributed and, in a preferred embodiment, a diaphragm disposed between the positive and negative electrodes.

The electrolytic cell has within it at least one positive and one negative electrode. These are disposed within the cell so as to be in contact with the electrolyte in which is distributed the porous bed of particulate material. These electrodes may be formed of various materials, as are known to those in the art. Typical of suitable electrode materials which may be used are graphite; noble metals and their alloys, such as platinum, iridium, ruthenium dioxide, and the like, both as such and as deposits on a base metal such as titanium, tantalum, and the like; conductive compounds such as lead dioxide, manganese dioxide, and the like; metals, such as cobalt, nickel, copper, tungsten bronzes, and the like; and refractory metal compounds, such as the nitrides and borides of tantalum, titanium, zirconium, and the like.

The positive and negative electrodes will be positioned within the electrolytic cell so as to be separated sufficiently to permit the flow of the electrolyte through the cell and the movement of the particle within the electrolyte. It will be appreciated, of course, that as the separation between the electrodes is increased, the voltage necessary to effect the desired reduction in the hexavalent chromium content of the electrolyte will also increase. Accordingly, in many instances it has been found to be desirable if the separation between the positive and negative electrode in the cell is from about 0.1 to 5.0 centimeters, with a separation of from about 0.3 to about 3.0 centimeters being preferred and a separation of from about 0.5 to 2.0 centimeters being particularly preferred. Although particular reference has been made to an electrolytic cell having one positive and one negative electrode, it will be appreciated that the cell may be provided with a plurality of electrode pairs, in much the same manner that such a plurality of electrodes are normally utilized in various commercial, large scale electrolytic continuous processes.

It will, of course, be appreciated that in addition to the amount of electrode separation, the flow of the electrolyte through the electrode area will also be dependent upon the size and density of the particles which are distributed in the electrolyte to form the porous bed. Typically, this flow, which is described in terms of the linear flow velocity of the electrolyte, will be within the range of from about 0.1 to 1000 centimeters per second. A preferred electrolyte flow velocity has been found to be from about 0.5 to 100 centimeters per second with a flow velocity of from about 1 to 10 centimeters per second being specifically preferred. Under these operating conditions, current densities within the range of about 1.0 to 500 milliamps per square centimeter have been found to be typical of those which are utilized.

In many instances it has been found to be preferred if the cell is provided with a diaphragm, disposed between the positive and negative electrodes. This diaphragm may be of various materials such as a Teflon® coated screen, Fiberglas®, asbestos, porous ceramics, and the like. The important criteria for the materials of which these diaphragms are made are that they permit the passage of the hexavalent chromium ions and are not adversely affected by the solutions being treated. In regard to the former, it is believed that the reduction in hexavalent chromium content is effected in the present process by the reduction of the Cr^{+6} to Cr^{+3} at the cathode and the subsequent precipitation of the Cr^{+3}, probably as a trivalent chromium hydroxide. Thus, the diaphgram serves not only to control the particles in the anode and/or cathode compartments of the cell but, additionally it helps minimize the back migration of the Cr^{+3} to the anode where it would be oxidized to Cr^{+6}. It is for this reason, that in many instances it has been found that increased reduction in the hexavalent chromium content may be obtained when a diaphragm is used. Depending upon the particular makeup of the solution being treated, its pH and temperature, however, satisfactory reduction of the hexavalent chromium content can also be obtained without a diaphragm in some instances.

Additionally, a suitable filter is desirably provided, through which the electrolyte solution is passed after being treated in the cell. In this manner, the precipitated chromium materials are removed from the solution either before it is disposed of or passed through the cell again for further treatment. This filter may be of any suitable size and material which will be effective in removing the precipitate without being adversely affected by the solution.

To further illustrate the present invention, reference is made to the accompanying drawing which is a schematic diagram of a system incorporating the electrolytic cell of the invention. As shown in the drawing, this system includes an electrolytic cell **1** having fluid inlets **6** and **14** and fluid outlets **9** and **16**. Within the cell **1** are disposed a positive electrode **2** and a negative electrode **3**. These electrodes are shown as being separated by a diaphragm **4**, although in some instances, the use of such a diaphragm may not be necessary. An electrolyte **8** is provided within the cell, which electrolyte is a solution containing hexavalent chromium material. Sources **5** and **15** of this electrolyte are provided, from which the electrolyte may be introduced into the cell through the inlets **6** and **14**. Distributed within the electrolyte **8** are particles **7**, which particles are distributed randomly through the electrolyte, the nature of the distribution depending upon the electrolyte flow, size and density of the particles, density of the electrolyte, and the like. The electrolyte **8** is pumped into the cell **1** through the inlets **6** and **14** from the electrolyte sources **5** and **15** and exits from the cell through the outlets **9** and **16** for recirculation through lines **12** and **20** or for subsequent processing through lines **13** and **19**, as is desired. Filters **17** and **18** are provided in outlet lines **9** and **16** which remove

any particles or precipitate formed in the electrolyte before it is recycled or subjected to further processing. The cell is further provided with screens **10** and **11**, screen **11** serving to support the particles in the cell and screen **10** serving to maintain the particles within the cell and prevent their discharge through the outlets **9** and **16**. As the distance between the screens **10** and **11** is changed, the volume of that portion of the cell in which the particles are distributed will likewise vary, thus, varying the porosity of the bed of particles which is maintained within the cell. Additionally, if desired, a single or common reservoir or source for the electrolyte solution may be used, rather than the dual sources **5** and **15** shown.

While it is not intended to restrict the operability of the present invention by any theory of operation, the use of particles in an electrolytic cell in the manner which has been described, has been found to have the following advantages. In a conventional electrolytic cell, such as a chlor-alkali cell, the amount of electrode surface at which the electrolytic reaction is conducted is dependent upon the surface area of the electrodes. Typically, this surface area will be about 1.3 times 10^5 cm^2. With a typical cell volume of about 3.5 times 10^6 $cm.^3$, the resulting ratio of the electrode area per cell volume is about 0.037 $cm.^2/cm.^3$. By the use of conductive particles in an electrolytic reaction, as in the process of the present invention, there is a significant increase in the surface area at which the electrolytic reaction may occur. In Chemical and Process Engineering, February 1968, page 93, there is described a cell containing an electrolyte having particles therein. It was calculated that the electrolyte containing the particles has an electrode area of about 11,500 $cm.^2$ and that the volume of the cell is about 153 $cm.^3$. This gives a ratio of electrode area to cell volume of about 75 $cm.^2/cm.^3$ which, clearly, is significantly higher than that of an electrolytic cell having conventional electrodes.

Additionally, it is believed that by the use of the particles in the electrochemical reaction, a mass transport phenomena may be taking place. In this, the contact of hexavalent chromium materials with the particles and electrodes is dependent upon a number of variables, including the electrolyte flow rate, the particle size, density and type, and the concentration of the hexavalent chromium material. From a consideration of all of the above variables, it has been found that the one condition which has an effect upon all of them is the porosity of the bed of particles and that this porosity, as defined hereinabove, is the determining factor that makes possible a commercially feasible operation.

Moreover, as has been indicated hereinabove, in the process of the present invention, the removal of the hexavalent chromium contaminates from the solutions treated is believed to be effected by cathodic reduction of the Cr^{+6} to Cr^{+3}. The Cr^{+3} materials form a precipitate, probably a trivalent chromium hydroxide, which is removed from the solution in any convenient manner, such as filtration, settling, centrifuging or the like. Thus, in this process, it has been found that little, if any, of the hexavalent chromium is removed from the solution by being plated out on the electrodes and/or particles of the porous bed as chromium metal.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. In these examples, unless otherwise indicated, temperatures are in degrees centigrade and parts and percent are by weight. It is to be appreciated, however, that these examples are merely exemplary of the present invention and the manner in which it may be practiced and are not to be taken as a limitation thereof.

In the following examples, an aqueous chrome plating bath solution was used. This solution, which initially contained 44.4 ounces/gallon CrO_3, 0.2 ounces/gallon Cr^{+3} and 0.3 ounces/gallon $SO_4^=$ and had a pH of 0.6, was diluted with water to form a solution containing 200 parts/million Cr^{+6} and 200 parts/million Cr^{+3} and having a pH of about 2.5. In each example, 700 cubic centimeters of this solution were circulated through apparatus similar to that shown in the drawing with the exception that the electrolytic cell did not contain a diaphragm. The solution was circulated for 15 minutes to allow for equilibration and a 50 cc. sample was withdrawn and analyzed for hexavalent chromium content and pH. The solution was then electrolyzed under the conditions indicated in the following table. Thereafter, the electrolyte was again analyzed for Cr^{+6} content and pH. The Cr^{+6} content of the solution was measured polarographically and the total chromium content of the solution was determined by atomic absorption. The anode used was graphite, the cathode nickel and the separation between the anode and cathode was 0.4 centimeters. Except where otherwise indicated, the particles used were graphite, having a particle size of 590 to 840 microns, the flow velocity was 0.7 centimeters/second and the bed porosity was 70%. In those examples having an initial pH above 2.4–3.0, NaOH was added to the solution to adjust the pH to the values shown. In all examples, the initial Cr^{+6} content of the solution was 200 parts/million. Using this procedure, the following results were obtained:

Example	Current density (milliamps/ $cm.^2$)	Time of electrolysis (minutes)	Initial pH	Final pH	Final Cr^{+6} content (parts/ million)
1[a]	15	50	2.9	3.6	297
2	15	420	10.0	5.8	3
3	23	240	10.1	6.5	18
4[b]	30	190	3.0	6.1	127
5	30	180	2.4	6.5	7
6	30	250	10.2	6.6	5
7	30	240	7.0	6.6	3
8	30	120	12.7	12.7	201

[a] No particles used. Flow velocity=3.2 cm./sec.
[b] Particles used were glass beads having a size of 500 microns. Flow velocity was 3.2 cm./sec. and bed porosity was 55%.

The procedure of the preceding examples was repeated with the exception that the electrolytic cell contained a Fiberglas® diaphragm, as shown in the drawing, and 700 cc. of the solution were circulated through both the anolyte and catholyte compartments. Using this procedure, the following results were obtained:

Example	Current density (milliamps/ $cm.^2$)	Time of electrolysis (minutes)	Initial pH	Final pH	Final Cr^{+6} content (parts/ million)
9[a]	15	210	6.9	6.6	4.8
10[a]	30	180	6.9	7.5	1.1
11	30	180	[b]6.7	6.0	2.2
			[c]6.7	9.9	0.4

[a] A common electrolyte source or reservoir was used in these examples.
[b] Anolyte. [c] Catholyte.

From all of the above results, it can be seen that although appreciable reductions in the hexavalent chromium content are obtained in many instances where a diaphragm is not used, the reduction is consistently lower with a diaphragm, particularly where the electrolyte pH is relatively high. It is for this reason that in the most preferred embodiment of the present process a diaphragm is used. It is to be noted that the increase in the final Cr^{+6} content in Examples 1 and 8, over the 200 parts/million initially present, is believed to have been caused by the anodic oxidation of some of the Cr^{+3} present to Cr^{+6}, which the absence of a diaphragm permitted.

While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention, as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is intended to be understood as referring to all equivalent elements for accomplishing substantially the same result in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A method for decreasing the hexavalent chromium content of a solution which comprises passing electric current through a solution containing a hexavalent chromium material, which solution is contained as an electrolyte in a cell, said cell having at least one positive and one negative electrode between which the current is passed, and wherein the electrolyte also contains a bed of dispersed particles, distributed therein such that the porosity of the bed is from about 40 to 80%, porosity being defined as:

$$\left(1-\frac{\text{volume of particles}}{\text{volume of cell wherein the particles are distributed}}\right)\times 100$$

cathodically reducing hexavalent chromium material in the solution to trivalent chromium material, forming a precipitate of the trivalent chromium material and removing said precipitate from the solution.

2. The method as claimed in claim 1 wherein the electrolyte solution is an aqueous solution.

3. The method as claimed in claim 2 wherein the initial concentration of the hexavalent chromium material in the electrolyte solution is from about 1 part per million to 10% by weight.

4. The method as claimed in claim 3 wherein the positive and negative electrodes in the cell are separated by a diaphragm.

5. The method as claimed in claim 1 wherein the particles distributed in the electrolyte solution have a density which is greater than that of the electrolyte.

6. The method as claimed in claim 1 wherein the particles distributed in the electrolyte solution are conductive particles.

7. The method as claimed in claim 6 wherein the particles are graphite.

8. The method as claimed in claim 1 wherein the particles are distributed within the electrolyte by flowing the electrolyte through the electrolytic cell in a direction opposed to the gravitational forces.

9. The method as claimed in claim 8 wherein the electrolyte flow velocity through the cell is from about 0.1 to 1000 centimeters per second.

10. The method as claimed in claim 1 wherein the electrolyte solution has a pH of from about 1 to 14.

11. The method as claimed in claim 10 wherein the electrolyte solution has a pH of from about 5 to 10.

12. The method as claimed in claim 1 wherein the porosity of the bed of particles is from about 55 to 75%.

13. The method as claimed in claim 12 wherein the porosity of the bed of particles is from about 60 to 70%.

14. The method as claimed in claim 1 wherein the separation between the positive and negative electrode within the cell is from about 0.1 to 5.0 centimeters.

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