

Review

Soil washing for metal removal: A review of physical/chemical technologies and field applications

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Abstract

Soil washing is one of the few permanent treatment alternatives to remove metal contaminants from soils. This paper reviews the various technology types and pilot/full-scale field applications of soil washing applicable to soils highly contaminated with heavy metals. The physical separation technologies, the chemical extraction processes and the integrated processes that combine both physical and chemical methods are discussed separately. This paper reviews basic principles, applicability, advantages and limitations, methods of predicting and improving performance of each physical/chemical technology. The discussion is based on a review of 30 recent laboratory investigations and 37 field applications of soil washing systems which have been undertaken, mostly in the US, for the period 1990–2007. This paper also examines and compares the status of soil washing technology for remediation of soils contaminated with metals in the US, in Canada and in Europe.

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Keywords: Heavy metals; Soil washing; Physical separation; Chemical extraction

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1. Introduction

In the United States, heavy metals are prevalent at almost all sites targeted by major remediation programs. For instance, metals are present in 77% of the Superfund sites (National Priorities List), in 72% of the Department of Defense (DOD) sites and in 55% of the Department of Energy (DOE) sites [1]. The USEPA estimates that over 50 million cubic meters of soil at current NPL sites are contaminated with metals [1].

The remediation of metal-contaminated sites has traditionally involved excavation of the contaminated soils, followed by the immobilization of metal contaminants by solidification/stabilization (S/S) technology prior to disposal of the materials treated in a permitted landfill site or on-site [2,3]. The remedial actions based on S/S technology are no longer considered a permanent environmental solution because of: (1) the metals are not removed from contaminated media; (2) the need for future monitoring of heavy metals on site; (3) questionable longevity of the solidified/stabilized materials; and (4) the long-term management of the solidified/stabilized materials is based on landfilling and requires soil caps to prevent erosion problems. Hence, there is a great need to promote effective soil treatment technologies that attempts to remove the metals from the soils. Soil washing, which uses physical or chemical processes, is one of the few permanent treatment alternatives to separate the metals from soils.

This paper provides a review of the soil washing methods (ex situ techniques) for soil contaminated with arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). Although arsenic is a metalloid, the term “metals” will be used to include all the elements under discussion. The discussion focuses on the remediation of soil matrices highly affected by industrial and military activities (e.g., soil contaminated by tailings/slugs, brownfields, battery recycling site, and shooting range site). Soil washing processes related to organic contaminants and radioactive metals are not discussed here. Also, the discussion does not include in situ treatment (soil flushing). In this review, soil washing includes the following options: (1) physical separation based on mineral processing technologies; (2) chemical extraction based on leaching or dissolving process; and (3) combination of physical separation and chemical extraction.

This paper is organized in five sections: (1) soil washing background; (2) physical separation; (3) chemical extraction; (4) combination of physical separation and chemical extraction; and (5) status of soil washing in the US, in Canada and in Europe. The

first purpose of this review is to present a technical description of the various technologies: principle, applicability, methods of predicting and improving performance are discussed. Several recent laboratory studies involving physical separation (seven examples) and chemical extractions (24 examples) are summarized. The physical separation technologies, the chemical extraction processes and the integrated processes that combine both physical and chemical methods will be discussed separately. The second purpose of this paper is to provide a review of the field applications of soil washing systems involved in the treatment of the metal contamination. The discussion is based on a collection of 37 case studies of pilot/full-scale remediation projects performed, mostly in the US, for the period 1990–2007. The third purpose of this paper is to review the implementation degree of soil washing technology relevant to the treatment of metal-contaminated soils, in the US, in Canada and in Europe.

2. Soil washing background

Soil washing, as discussed in this paper, refers to ex situ techniques that employ physical and/or chemical procedures to extract metals contaminants from soils. Fig. 1 presents a schematic diagram of typical options used in soil washing processes: (1) physical separation; (2) chemical extraction; (3) combination of both. Physical separation (PS) concentrates metal contaminants into a smaller volume of soil by exploiting differences in certain physical characteristics between the metal-bearing particles and soil particles (size, density, magnetism, and hydrophobic surface properties). Chemical extraction (CE) relates to techniques that try to solubilize the metal contaminants from the soil with an extracting aqueous fluid containing chemical reagents such as acids or chelating agents.

Soil washing systems are quite flexible in terms of number, type, and order of processes involved and other names are used for soil washing technologies: “soil separation”, “soil recycling”, or “volume reduction”. The definition and use of the terms “soil washing”, “physical separation” and “chemical extraction” can differ according to the authors. The degree to which chemical agent or physical separation techniques are used may affect the nomenclature to describe the washing process. In the US and in Europe, soil remediation processes based on mineral processing technologies are often referred as the broad term “soil washing” [4–6] although the term “physical separation” appears more accurate [7–9]. The term “soil washing” is also used in the literature for describing processes that involve chemical extraction processes [10–13]. FRTR [4] distinguishes “soil

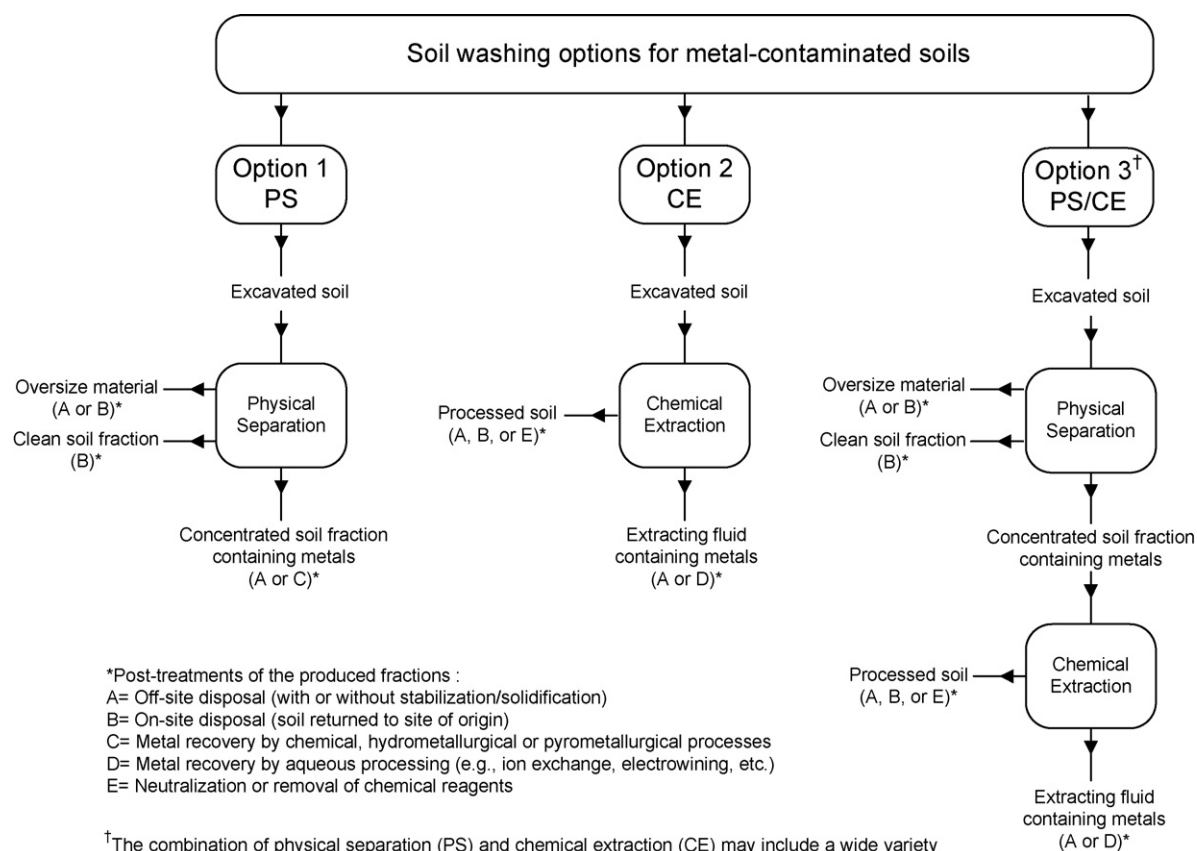


Fig. 1. Schematic diagram of typical options used in soil washing processes.

washing” from “chemical extraction”: «soil washing generally uses water or water with wash-improving additives and differs from chemical extraction, which uses an extracting chemical». Confusion resulting from these misnomers often contributes to the propagation of misconceptions about the soil washing technology.

In the present paper, physical separation is primarily considered as a particle separation process while chemical extraction can be considered as a metal desorption/solubilization process. In general, physical separation is primarily applicable when metal contaminants are under particulate forms (ideally liberated particle), while chemical extraction is primarily suitable for ionic forms adsorbed on soil or non-detrital metals. Specific comments relating to these aspects are provided in the corresponding sections of each technique.

The authors collected information on full-scale and significant pilot/field demonstrations of soil washing projects conducted in the US and Canada for treating metal contaminants. Also, some pilot projects performed in Europe and Korea are gathered. Table 1 recapitulates 37 field application case studies: 16 projects involved PS technologies, 18 projects involved both PS and CE processes, and three projects involved CE procedures. About one third of the reported projects have been performed since the year 2000. The metals most frequently treated are: Pb (78% of the projects), Cu (43%), Zn (41%), and As (27%). For each project, Table 1 summarizes the following data: (1) the

project description (location, site name, the matrix type treated, and completion date); (2) the basic principle and an exhaustive description of the process; (3) the metal concentrations in the initial soil and the cleaned soil; (4) the removal efficiencies of the treated metals; (5) the volume capacity of the process; (6) the treated volume; and (7) the quantities of the recovered metals/concentrates, the management of the recovered metals and washing residuals, and volume reduction efficiency. These data are used as support for the overall discussion.

3. Physical separation technologies

The general approach in physical separation is to use technologies generally applied in mining and the mineral processing industry to extract the desired metal-bearing particles from mineral ores. Mineral processing techniques are well established: implementation is relatively simple; operation is often inexpensive; equipments and processes involved are well described in the literature [14,15]. In the context of soil remediation, mineral processing technologies were reviewed particularly to separate metal contaminants from the soil [8,9,16,17]. Table 2 summarizes the main classes of technologies according to the separation principles used. The operation units involved are: mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, electrostatic separation, and attrition scrubbing.

Table 1
Field applications of soil washing technologies

#	Project description (status, location, remediation sponsor/vendor, and completion date)	M/F ^a	Type ^b	Technology description	Metal	Initial ^c ($\mu\text{g/g}$)	Final ^c ($\mu\text{g/g}$)	RE ^d (%)	Cap. ^e	Vol. ^f	Metal recovery/recycling, management of the processed soil and washing residuals	Ref.
1	Pilot-scale demonstration of transportable unit at PPG Canada Inc. site in Beauharnois, QC, Canada (1992)	M	PS	Screening, gravity concentration, hydrocyclone, froth flotation	Hg	>1000	624	25–50	3 m ³ /h	5,000 m ³	Hg recycling (1.3 t of Hg were recovered)	[103]
2	Pilot-scale demonstration (Environment Canada program) of Tallon's physical separation unit at Dickson site, Montreal, QC, Canada (1993)	M	PS	Vibrating screen, magnetic separation, attrition scrubbing, froth flotation	As Cu Pb	27–52 115–366 248–336	14–21 100–347 188–327	50–60 <25 <25	300 t/day	–	–	[37]
3	Full-scale application performed by Alternative Remediation Technologies (ART) at King of Prussia Superfund site, NJ (1993)	M	PS	Wet screening, hydrocyclones, attrition scrubbing, froth flotation	Cr Cu Ni	500–5500 800–8500 300–3500	73 110 25	>90 >90 >90	30 t/h	19,200 t	85% of soil was re-deposited on site; revegetation; sludge cake (2000–6000 $\mu\text{g/g}$ of metals) was disposed off-site	[6,104]
4	SITE demonstration of BESCORP (Brice Environmental Service) plant system at the Alaskan Battery Enterprises site, Fairbanks, AK (1993)	F	PS	Wet screening, attrition scrubbing, density separator	Pb	5600	200	65–85	20 t/h	56,000 t	Disposal; Pb recycling (Pb smelter)	[105]
5	SITE demonstration of physical separation coupled with thermal desorption system (Harbauer GmbH & Co. KG, Berlin) for remediation of soils from Marktredwitz site, Germany (1996)	F	PS	Crushing, screening, attrition scrubbing, hydroclassification	Hg	780–1080	17	98	4–20 t/h	63 t	Hg recovery: thermal desorption (vacuum-distillation)	[106]
6	Field application performed by Metcalf & Eddy for remediation of Naval Weapons Station Earle Pistol Range, NJ (1996)	M	PS	Size and density separation	Pb	>20,000	14–92	>90	–	1,500 t	Pb recycling (10 t of recovered bullet); 70 t of clay fines required recycling at an asphalt batch plant	[21]
7	Full-scale application performed by ART and CINTEC for remediation of soils from seven brownfields in Montreal, Qc, Canada (1996)	F	PS	Screening, hydrocyclones, froth flotation	Cu Pb Zn	200–10,000 700–3000 1000–5000	–	–	30 t/h	22,300 t	Some site soils, which were not feasible for treatment by soil washing, were disposed directly at the Cintec landfill	[6,107]
8	Pilot-scale demonstration of the physical separation process (INRS and Dragage Verreault Inc.) for remediation of brownfield soils from Montreal, QC, Canada (2000)	F	PS	Screening, fluidized-bed separation, gravity separators (jigs, spiral conc., MGS-Mosley), froth flotation	Cu Pb Zn	675–950 466–994 1869–2293	321–419 399–466 1483–1793	52–56 26–60 21–22	–	10 t	Soil fraction <6 mm was treated; the cleaned soil fraction was 85% of initial soil	[22]

9	Several full-scale applications of Kuryluk Mineral Separator (KMS) concentrator (Phase Remediation Inc.) in Europe (2000)	-	PS	Gravity separator (KMS concentrator)	Cu Pb Zn	-	-	-	-	-		[108]
10	Full-scale application of BESCORP's Particle Separation System, performed on Pb-contaminated soils from the SAFR site at range 24, Fort Dix, NJ (1999)	M	PS	Grizzly, vibrating wet screen, hydrocyclone, gravity separation by jig	Pb	5300-38,000	396	93	-	3,600 t	Recovering spent bullets and Pb recycling (21 t of Pb 95% purity) for Pb-smelter; 100% of soil suitable for reuse	[109,110]
11	Full-scale application of BESCORP's Particle Separation System, performed on soils from the SAFR site at Massachusetts Military Reservation (MMR), Cape Cod, MA (1999)	M	PS	Screening, hydrocyclone, gravity separation by jig	Pb	>4820	<TCLP	98	-	6,200 t	Pb recycling (50 t of spent bullet) for manufacturing batteries; 601 t of residual soil was stabilized; 90% of soil suitable for reuse; revegetation	[109,110]
12	Full-scale application of BESCORP's Particle Separation System at the SAFR complex of Marine Corps Air Ground Combat Center, 29 Palms, CA (1998)	M	PS	Screening, hydrocyclone, gravity separation by jig	Pb	20,000	1600	89	250 t/day	12,000 t	Pb recycling (240 t of Pb 94% purity); 100% of soil suitable for reuse	[109,110]
13	Full-scale application of ART's Process at Former Skeet Shooting Range Site (soil and sediment), Lordship Point in Stratford, CT (2000)	M	PS	Vibrating wet screen, hydrocyclones, gravity separation jig	Pb	-	-	-	100 t/h	30,000 m ³	Pb shot recovered (90% purity) was treated in off-site facility for Pb recycling; revegetation	[107]
14	NATO/CCMS Pilot test on decontamination of mercury-polluted site (267-445 t of Hg in 222.740 m ³ of soil) in Ústí nad Labem, Czech Republic (2000)	F	PS	Hydrocyclone, wet gravity separation	Hg	100-10,0000	<10	-	-	2 t	Hg recycling	[111]
15	Pilot-scale demonstration of BESCORP's Particle Separation System at the SAFR site, Fort Ord, CA (period 2001-2005)	M	PS	Grizzly, vibrating wet screen, hydrocyclone, gravity separation by jig	Pb Cu	2000 -	227 <100	95	400 t/day	400 t	Metal recycling	[109,110]
16	Full-scale application of ART's Process at Former Bend Trap Club Skeet Range, Bend, OR (2007)	M	PS	Screening, gravity separation by jig	As Pb	-	<400	~90	50 t/h	23,800 t	Pb recycling (110 t of upgraded Pb shot); 90% of soil was disposed on-site	[107]

Table 1 (Continued)

#	Project description (status, location, remediation sponsor/vendor, and completion date)	M/F ^a	Type ^b	Technology description	Metal	Initial ^c ($\mu\text{g/g}$)	Final ^c ($\mu\text{g/g}$)	RE ^d (%)	Cap. ^e	Vol. ^f	Metal recovery/recycling, management of the processed soil and washing residuals	Ref.
17	SITE demonstration of Toronto Harbour Commissioners (THC)/Bergmann USA for the remediation of the contaminated fine particles of soil from a former auto/metal salvage site, Port Industrial District, Toronto, ON, Canada (1992)	F	PS/CE	(1) PS: screening, hydrocyclones, attrition scrubbing, density separation; (2) CE: solubilization by acid leaching followed by ion exchange chelating resin	Cu Ni Pb Zn	1223 469 1687 3072	169 84 211 211	86 82 87 93	50 t/h	820 t	Metal recovery in metallic forms by electrowinning	[112]
18	Field demonstration of physical separation techniques for remediation of soils from SAFR, conducted by US Bureau of Mines (1993)	–	PS/CE	(1) PS: screening, hydrocyclone, gravity concentration (jig, spirals conc., Bartles-Mozley table); (2) CE: heap acid leaching	Pb	100,000	–	>90	–	–	Pb concentrate can be sent to Pb smelter; No data about % of cleaned soil	[8]
19	Field demonstration of physical separation to remove Hg from soils, conducted by MRSDI for Energy and Environmental Research Center (EERC) (1994)	–	PS/CE	(1) PS: vibrating screen, gravity concentration (Neffco concentrator and spirals); (2) CE: acid leaching	Hg(s) ^g Hg(c) ^g	15,370 920	10 33	80–99 30–96	–	–	RE are given for PS and CE, respectively; Hg recycling (600 g of Hg element was recovered)	[8]
20	Field-scale application of BESCORP and COGNIS systems at Twin Cities Army Ammunition Plant, Site F in New Brighton, MI (1994)	M	PS/CE	(1) PS: BESCORP process (trommel and wet classifier, density separation by jigs); (2) CE: COGNIS Terramet [®] (acid) leaching process for fine particles	Pb	380–86,000	<200	>75	15 t/h	400 t	PS process reduced the Pb load to the CE process by 39% to 63%; Pb concentrates from jigs and CE processes were transported to Pb smelter	[113]
21	Pilot plant demonstration (Environment Canada and MCEBR program) of a metal-separation process developed by Alex-Sol Inc. and INRS for remediation of soils and sediments from Quebec city, Montreal, and Trois-rivieres, Canada (1995)	F	PS/CE	(1) PS: density separation, magnetism separation and froth flotation; (2) CE or bioleaching	Cu Cd Pb Zn	117–7533 1020 1202–2595 1521–22,800	34–402 <5 591–877 333–791	48–98 99 51–69 68–99	–	45 t	Potential for reuse of processed soil or sediments; potential for recovery of extracted metals	[114]
22	Field demonstration of BESCORP's soil washing process at Joint Small-Arms Range 5, Fort Polk, Leesville, LO (1996)	M	PS/CE	(1) PS: attrition, size screening, hydrocyclones, density separation by jig; (2) CE: acid leaching (HCl)	Pb Cu Zn	4117 – –	165 – –	90 97 89	6 t/h	835 t	67% and 32% of soil suitable for reuse after PS and CE, respectively; Pb recycling (9 t) by Pb-smelting	[41]

23	Field demonstration of ContraCon Northwest's soil washing process at Joint Small-Arms Range 5, Fort Polk, Leesville, LO (1996)	M	PS/CE	(1) PS: attrition, size screening, hydrocyclones, density separation by jig; (2) CE: acetic acid leaching	Pb Cu Zn	2828 – –	122–1443 – –	93 93 77	3 t/h	263 t	The processed soil was unsuitable for return to the site (due to inadequate neutralization and failed TCLP) and was sent to a landfill	[41]
24	Pilot-scale demonstration of soil washing performed by Metcalf & Eddy at explosives manufacturing, location unknown (1996)	M	PS/CE	(1) PS: size/density separation; (2) CE: acid leaching	As Pb	97–227 3500–6300	7–142 10–306	34–93 95–99	–	200 t	–	[115]
25	Full-scale application of soil washing system of Tallon Metal Technologies Inc. at the Longue Pointe site in Montreal, QC, Canada (reported in 1998)	M	PS/CE	(1) PS: screening, gravity and magnetic separation; (2) CE: hydrometallurgical extraction and Vitrokele™ adsorption	Pb	11,800 max	<1000	93	600 t/day	150,000 t	95% of processed soil suitable for reuse; potential recycling of Pb concentrates	[100,116]
26	Pilot-scale demonstration of soil washing system of Tallon Metal Technologies at the Ataratiri site in Toronto, ON, Canada (reported in 1998)	M	PS/CE	(1) PS: screening, gravity and magnetic separation; (2) CE: hydrometallurgical extraction and Vitrokele™ adsorption	Cd Cu Pb Zn	4 950 2112 2535	<1 290 898 286	90 70 57 67	600 t/day	35 t	Potential recycling for recovered metal; 85% of soil was recovered for reuse	[100,116]
27	Field demonstration of the soil washing system at Hunter's Point Shipyard, San Francisco, CA (1998)	–	PS/CE	(1) PS: fluidized bed separation; (2) CE: acid leaching	Cu, Cr Pb, Zn	–	–	–	–	–	–	[117]
28	Full-scale application (results of pilot demonstration) of biogenesis sediment washing technology for remediation of dredged materials (90% silt/clay) from the New York/New Jersey Harbor (1999–2001) ^b	0–	PS/CE	(1) Washing with high pressure water and surfactants/chelating agents (metal separation) in collision chamber; (2) hydrocyclone and wet screen	As Cd Pb Zn Hg	12.3 3.1 157 279 3.9	7.8 1.2 68 131 0.3	36 61 57 53 92	30 m ³ /h	200,000 m ³ /year	Potential reuse of decontaminated sediment; further treatment of washing solution (metal precipitation)	[118]
29	Pilot soil washing/leaching test for remediation of soils from battery-breaking site in Fairbanks, AK (2001)	M	PS/CE	(1) PS: size separation, density separation by jig; (2) CE: leaching with chloride solution (NaCl, 2 M; HCl, pH 2) and oxidant (NaOCl)	PS:Pb ⁱ CE:Pb ⁱ	750 2300	87–117 84	84–88 96	–	40 t	85% and 5% of soil was cleaned with PS and CE, respectively (VR = 90%); jig concentrate was 2.7 t; metal recovery by PbS precipitation; PbS cake can be sent to smelter	[70]

Table 1 (Continued)

#	Project description (status, location, remediation sponsor/vendor, and completion date)	M/F ^a	Type ^b	Technology description	Metal	Initial ^c (µg/g)	Final ^c (µg/g)	RE ^d (%)	Cap. ^e	Vol. ^f	Metal recovery/recycling, management of the processed soil and washing residuals	Ref.
30	Pilot soil washing/leaching test for remediation of soils from SAFR site, DE (2001)	M	PS/CE	(1) PS: size separation, density separation by jig; (2) CE: leaching with chloride solution (NaCl, 2 M; HCl, pH 2) and oxidant (NaOCl)	PS:Pb ⁱ CE:Pb ⁱ	5721 830	139–342 81	94–98 90	–	13 t	29% and 62% of soil was cleaned with PS and CE, respectively (VR = 91%); jig concentrate was 1.2 t; metal recovery by PbS precipitation; PbS cake can be sent to smelter	[70]
31	Pilot-scale demonstration of the BioGenesis sediment decontamination process for remediation of dredged materials from the lagoon of Venice, Italy (2005) ^h	F	PS/CE	(1) Washing with high pressure water and surfactants/chelating agents in collision chamber; (2) hydrocyclone and wet screen	As Cd Cu Pb Zn Hg	16–73 6–41 95–375 40–531 115–531 3–10	6–15 1–9 17–39 27–138 84–630 0.5–2	6–85 0–83 60–91 0–74 0–72 75–93	15 m ³ /h	330 m ³	Precipitation of metals from washing solution; Fine fraction of treated sediment, which has higher metal concentrations, was disposed to a landfill site	[119]
32	Pilot-scale study for remediation of contaminated soils from mining area, Seoul, Korea (2006)	M	PS/CE	(1) Attrition scrubbing chemically enhanced by acid leaching (HCl, H ₂ SO ₄ , or H ₃ PO ₄) in drum-type scrubber; (2) separation of fine soil + wastewater and sand soil	As Ni Zn	43 340 68	10–15 140–145 50–55	63–75 59–60 38–45	Batch (40 kg)	0.5 t	VR = 51–98% (vary according to particle size fraction); the fine soil fraction (highly contaminated) requires further treatment	[45]
33	Pilot plant demonstration for remediation of urban contaminated soil from Québec city, Canada (2007)	M	PS/CE	(1) PS: size separation (screening, spiral, hydrocyclone); (2) CE: acid leaching (HCl, pH 2–3)	Cu Pb Zn	202–350 2030–2200 870–960	40–234 69–848 111–941	44 60 52	–	30 t	The process produced 91% of a non-contaminated soil and 9% of metallic residue and heavily contaminated soil	[101]
34	Full-scale application of the ART's process at Vineland Chemical (Pesticide manufacturing) Superfund site, NJ (project in progress)	F	PS/CE	(1) PS: size screening, hydrocycloning; (2) CE: leaching and precipitation	As	20–5000	<20	–	70 t/h	350,000 t	Off-site disposal for filter cake residue containing high concentrations of As	[107,120]
35	Full-scale project of soil washing coupled with chemical treatment (chromium reduction) at Palmetto Wood Preserving, SC (1989)	M	CE	Batch washing process using sodium metaphosphate to lower pH to 2.0 and extract the chromium from the soil	As Cr	2–6200 4–6200	<1 627	99 90	–	10,000 m ³	Chemical treatment of leachate: reduction of Cr(VI) to precipitate in Cr(III) form; disposal of soil and sludges residual	[121]

36	SITE demonstration (bench- and pilot-scale) performed by Center for Hazardous Materials Research for remediation of four soils from US Superfund Sites (1995)	F	CE	Acid leaching (HCl, pH < 2)	As, Cd Cr, Cu Pb, Zn	Variable	50–95	5–10 t/h	–	RE is most lower for As; metals are concentrated in a form potentially suitable for recovery	[96]
37	NATO/CCMS Pilot test of the CACTIOX™ process to remediate soils with high clay and silt content, United Kingdom (1998)	F	CE	Mild leaching and extraction (oxidants, complexing agents, and organic acids)	Cr, Cu, Zn, Pb, Cd, As	Variable 1000–22,500 <Dutch B levels	50–70	10–100 kg/h	–	As and Cd > targeted by precipitation/ion exchange	[116]

–: not available; SAFR: small arms firing range; SITE: Superfund Innovative Technology Evaluation of USEPA; MCEBR: Montreal Centre of Excellence in Brownfields Rehabilitation; VR: volume reduction.

^a M: mobile system suitable for remediation on-site; F: the project has been performed in fixed facilities.

^b Basic principle of process; PS: physical separation; CE: chemical extraction.

^c Metal concentration: mean value or range, which may vary according to the tested samples or the particle size fractions that have been treated.

^d Removal efficiency of metal (the value is calculated from the concentrations or the recovered metal mass).

^e Capacity in tonnes metric per hour (t/h) or per day (t/day), cubic meters per hour (m³/h).

^f The treated volume.

^g The study distinguishes the treated soil fractions (s: sand, c: clay).

^h The description does not include the remediation process of the organic contaminants, which were destroyed by cavitation/oxidation after separation with surfactants.

ⁱ The study distinguishes the performances of the PS and CE processes.

Three aspects about physical separation for remediation of metal-contaminated soils will be separately discussed: (1) the applicability of physical separation technologies according to forms of metal contamination and characteristics of soil matrix; (2) a review of each technology class; and (3) integrated processes of physical separation. The discussion focuses first and foremost on gravity concentration and froth flotation technologies because they are the most important separation methods used in a soil remediation context. The arguments are often based on the assessment of the field-scale applications (Table 1) and recent laboratory investigations (Table 3).

3.1. Applicability and limitations of physical separation

Physical separation techniques are primarily applicable to particulate forms of metals: discrete particles or metal-bearing particles. Physical separation is generally not appropriate for treating the sorbed forms of metals although attrition scrubbing can significantly improve metal desorption in chemical leaching process. The knowledge of the degree of liberation of the mineralogical phase containing heavy metals is significant to predict the applicability of physical particle separation methods [16,18]. The liberation degree depends on the mineralogical aspects of metal contaminant particles (shape, morphology, and mineralogical association). Liberation degree refers to the release availability of the “metal phase” according to various associations with the “carrying phase” or the soil particles. The term “metal phase” refers to the mineral form under which the metal is present. The term “carrying phase” refers to another mineral phase (Fe-oxides, carbonates, silicates, etc.) with which the “metal phase” can be associated. Fig. 2 summarizes some examples of various potential states of the metal phase (particulate forms): (a) included in the volume, (b) associated, (c) weakly bounded on surface, and (d) liberated or free. Liberation degree and applicability of particle separation, by gravity concentration and froth flotation, are briefly discussed for each state of metal phase (Fig. 2). The mineralogical aspects and solid phase speciation of metal-bearing particles can be investigated by microscopy and spectroscopy technologies such as scanning electron microscope coupled with energy-dispersive X-ray analysis (SEM–EDX).

The efficiency of physical separation depends on several soil characteristics such as particle size distribution, particulate shape, clay content, moisture content, humic content, heterogeneity of soil matrix, difference in density between soil matrix and metal contaminants, magnetic properties, and hydrophobic properties of particle surface [8,9]. The treatment is difficult or unfeasible for the following cases: (1) the metal contaminants are strongly bound on soil particles; (2) the difference in density or surface properties between metal-bearing particles and soil matrix are not significant; (3) high variability of chemical forms of metals; (4) the metals are present in all particle size fractions of contaminated soil; (5) the soil contains silt/clay content in excess of 30–50%; (6) the soil contains high humic content; and (7) the soil contains organic compounds with high viscosity.

Particle size of feed material is one of the most significant parameters that affect applicability of physical separation tech-

Table 2
Summary of physical separation types

Operation unit	Basic principle	Description and main objectives	Comments	Typical technologies implemented
Mechanical screening	Separation based on particle size	Mechanical screening uses size exclusion through a physical barrier to provide suitable dimensions for treatment	Widely used. Fine screens are fragile	Vibrating grizzly; barrel trommel; vibrating or gyratory screens
Hydrodynamic classification	Separation based on settling velocity	Hydrodynamic classification separates the particles by difference of settling velocity or by centrifugal force into a water flow. These methods are often used for size separation	Widely used. Difficult when clay and humic soils are present	Hydrocyclones, elutriators, mechanical classifiers (screw classifier)
Gravity concentration	Separation based on density of particles	The gravity concentration technologies separate high density from low density minerals or particles in a slurry of water and soil (relatively high solid content)	Widely used. Difficult when clay and humic soils are present	Spiral concentrator, shaking table, jig, MGS-Mozley, dense media separation (DMS)
Froth flotation	Separation based on hydrophobic properties of the surface of particles	The differences in hydrophobic properties of particle surfaces are exploited to separate certain minerals from soil by attachment to air bubbles injected in a pulp (low solid content)	Widely used. Chemical additives are required	Flotation in cell or in column (agitation or nonagitation system)
Magnetic separation	Separation based on magnetic properties of particles	Mineral particles are separated according to their different magnetic susceptibilities	Moderately used. High capital and operating costs	Dry or wet separators using high intensity (HIMS) or low intensity (LIMS)
Electrostatic separation	Separation based on electrical conductivity properties of particles	The separation is based on the difference in the surface electrical conductivity of the particles to be separated	Rarely used. Materials must be completely dry	Electrostatic and electrodynamic separators
Attrition scrubbing	Mechanical particle-to-particle scrubbing	Attrition scrubbing uses high energy agitation of soil slurry (high solid content) to remove coating of particle surface and to disperse soil aggregates	Widely used. Pre-treatment that improves separation process	Various types of scrubbers

nologies because the contaminated soils usually contain a wide range of particle sizes, and the technology performance is often restricted to a specific particle size range (Fig. 3). Usually, most of the hydroclassifiers and gravity concentrators have a good applicability for the sand fraction (63–2000 μm). The standard gravity concentrators (jig, shaking table, and spiral) are usually not suitable for fine particles (<63 μm). Depending upon the technology, there is a point at which the percentage of fine particles will be a limiting factor. Physical separation is mainly appropriate and more cost effective for soils with sand content in excess of 50–70% [19,20]. However, a process combining attrition scrubbing (which can be enhanced by chemical additives) and wet screening or hydrocyclones may be used for the remediation of fine-grained matrices such as sediments [10]. Likewise, froth flotation may be effective for treating relatively fine particles (20–63 μm).

The selection of the physical separation technologies strongly depends on the soil and site types to be treated. These techniques are primarily applicable to “anthropogenic” soils located in urban or industrial areas (e.g., brownfields, mine spoils/tailings/slugs from mining/smelting sites, and shooting range site) (Table 1). These soils are greatly affected by human activity (industrial artifacts, disposal, landfills, etc.) and are typically composed of mixture of toxic wastes and

natural/anthropogenic landfills. On the other hand, physical separation techniques are not appropriate for treating the “natural” soils or agricultural soils affected by a diffuse contamination because: (1) the metals are mostly present in sorbed forms; (2) the metal concentration levels are relatively low; and (3) these soils typically have a high content of silt/clay and organic matter. Since metals present in soils are mostly in sorbed forms as opposed to discrete particles, physical separation is often associated with chemical procedures to enhance metal removal.

3.2. Hydrodynamic classification

Hydrodynamic classification, also called “hydroclassification”, involves separation of particles based upon the velocity with which particles fall through water flow (involving sedimentation, elutriation, and fluidization) or separation by centrifugal force into water flow (hydrocyclone) [8,16]. The main goal is separation by size particle. Hydrodynamic classification technologies principally include three technology classes: (1) technologies based on centrifugation such as hydrocyclones; (2) technologies based on elutriation such as elutriation column and fluidized-bed classifier; (3) mechanical classifiers such as screw classifier. Hydrocyclones were widely implemented in soil washing process to separate the fine soil from larger

Table 3
Laboratory investigations of physical separation technologies

Examples of studies	Study objective	Technologies (treated soil fractions)	Metal	Conc. ($\mu\text{g/g}$)	RE% ^a (technology or operating conditions)	VR% ^b	Ref.
Magnetic separation (HIMS) on six soils in the Netherlands (results with soil "L")	Use of magnetic separation as stand-alone remediation technique	High intensity magnetic separation (HIMS) with dry and wet separators (63–2000 μm)	Cu	126	83	87–93	[35]
			Cr	244	77		
			Pb	121	46		
			Zn	598	79		
Attrition scrubbing in conjunction with a shaking table on a soil from an Army small arms training range, USA	Improvement of density separation (shaking table) by the use of attrition scrubbing	Wemco attrition scrubber, Wifley shaking table	Pb	40,000	96	80	[43]
Evaluation of physical separation technologies for remediation of six brownfield soils (polluted by landfilling of various wastes in Quebec City, QC, Canada (results with soil "A1", 90% of sand)	Study of various physical separation technologies for an integrated soil washing process	Wet magnetic separator (63–2000 μm), Attrition scrubbing, gravity concentration: shaking table (63–850 μm); jig (850–2000 μm)	Cu	7,458	52 (jig)/89 (shaking table)	NA	[18]
			Pb	4,893	61 (jig)/67 (shaking table)		
			Zn	3,535	58 (jig)/54 (shaking table)		
Gravity separation to remediate two shooting range soils contaminated by Pb-containing shotgun pellets in Finland (results with Utti soil)	Study of applicability of gravity separation to remove bullet fragments	Shaking table, heavy liquid separation (DMS)	Cu	113,000	73 (DMS)/85 (DMS + shaking table)	80–90	[122]
			Pb	24,000	88 (DMS)/91 (DMS + shaking table)		
Evaluation and analysis of soil washing for seven Pb-contaminated soils from Netherlands	Evaluation of gravity separators in an integrated soil washing process	Shaking table (74–840 μm); jig (840–4760 μm)	Pb	500–2,195	22–93 ^c (jig + shaking table)	NA	[51]
Froth flotation as a remediation technique for heavily polluted sediment in Belgium	Evaluation of froth flotation as stand-alone remediation technique. The influence of the particle size distribution and metal speciation on the froth flotation efficiency	Denver laboratory cell (grain size: 70% <50 μm)	Cd	13	60 at pH 8	80	[25,26]
			Cr	267	48		
			Cu	128	53		
			Pb	721	60		
			Zn	3,200	60		
Froth flotation on a soil in Tienen, Belgium	Improvement of froth flotation by sulfidisation pre-treatment	Sulfidisation with Na ₂ S, Denver laboratory cell (0–2000 μm)	Cd	8	25 (without sulfi.)/47 (with sulfi.)	70–80	[28]
			Cu	68	30 (without sulfi.)/45 (with suldi.)		
			Pb	142	30 (without sulfi.)/42 (with suldi.)		
			Zn	357	30 (without sulfi.)/42 (with suldi.)		

^a Removal efficiency.

^b Volume reduction of contaminated soil.

^c Range value, according to soil types.

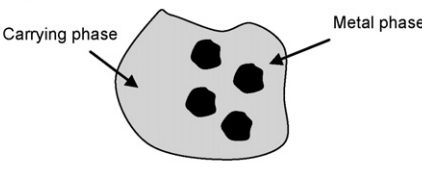
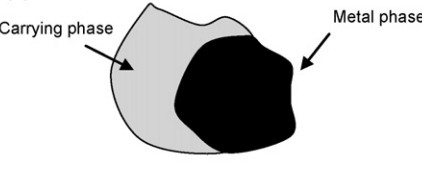
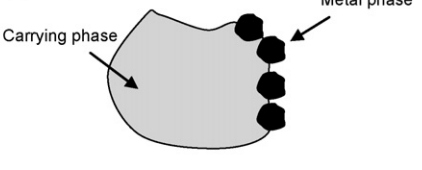

<p>(a)</p> 	<p>Metal phase included in volume</p> <ul style="list-style-type: none"> • Liberation degree is very low • Density depends primarily to minerals of carrying phase • Surface properties are constant but depend to carrying phase • Physical separation is very difficult or impossible • Crushing is required
<p>(b)</p> 	<p>Metal phase associated</p> <ul style="list-style-type: none"> • Liberation degree is medium • Density depends to minerals of metal phase and carrying phase • Surface properties are not constant • Physical separation can be applicable (gravity concentration)
<p>(c)</p> 	<p>Metal phase weakly bounded on surface</p> <ul style="list-style-type: none"> • Liberation degree is medium • Physical separation can be applicable if metal phase particles are liberated by e.g., attrition scrubbing
<p>(d)</p> 	<p>Metal phase liberated or free</p> <ul style="list-style-type: none"> • Liberation degree is very high • Density depends only to minerals of metal phase • Surface properties are constant • Physical separation is applicable (e.g., gravity concentration, froth flotation)

Fig. 2. Applicability of physical separation according to liberation degree of the metal phase for the particulate forms.

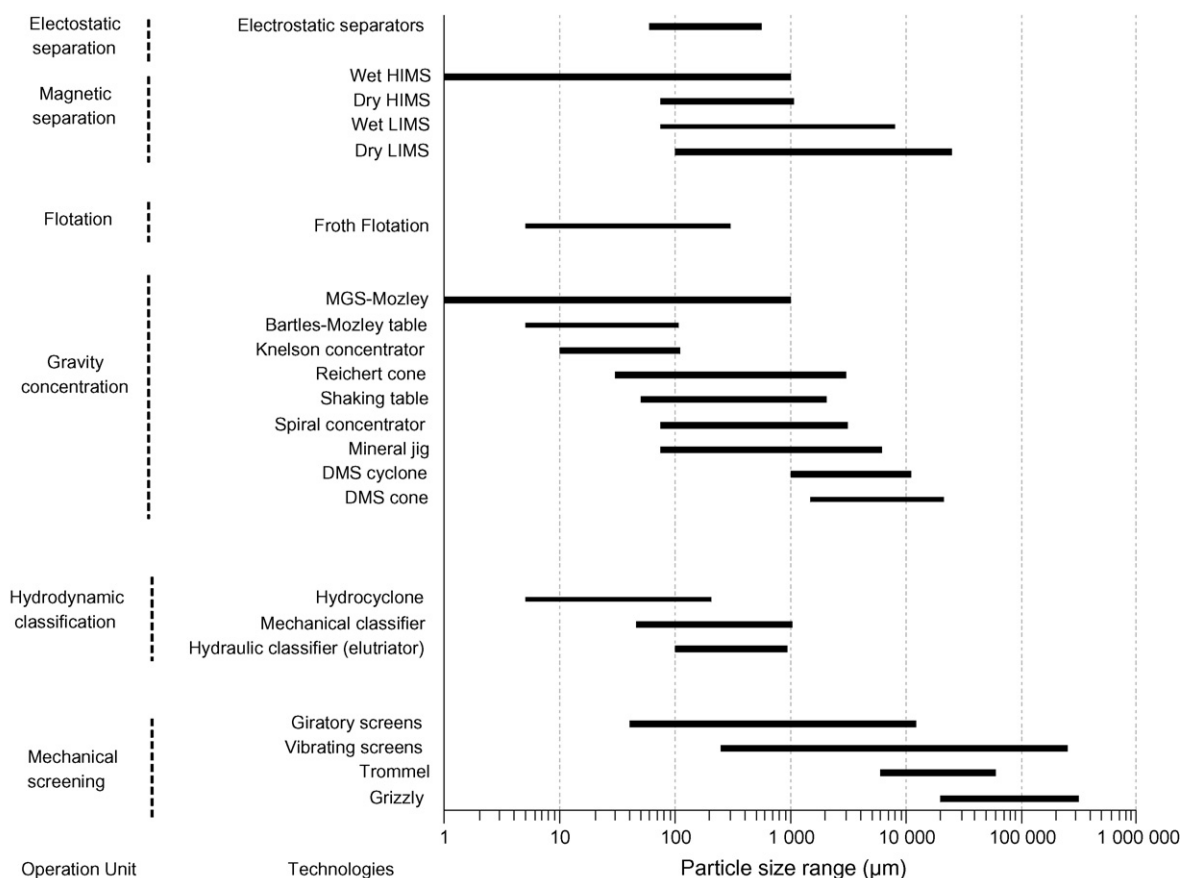
sand particles. The centrifugal force is more powerful than the force due to gravity; thereby, the operating time to achieve separation is significantly reduced [16]. Hydrocyclones have low capital and operational costs compared to other classification equipment [9]. Screw classifiers and hydroclassifiers based on elutriation can also be implemented in a soil remediation context [16,21,22]. Moreover, new more efficient technologies of fluidized-bed separator such as the CrossFlow classifier and the HydroFloat separator have recently been developed for the mineral processing industry [23].

3.3. Gravity concentration

These techniques exploit the difference in gravity of particles in slurry to separate the metal-bearing particles from soil matrix. Settling is due to density, size, shape and weight of particle; however, density is the key factor. Gravity separation is inefficient when used to treat particles that have either a wide size distribution or a narrow density distribution [9]. Gosselin et al. [16] report that density difference must be greater than 1 g/cm^3 for sufficient separation. The effectiveness of density separation can be estimated by the “concentration criterion” from Taggart [8,14]. The gravity concentrators such as jig, shaking table and spirals can be affected by particle size effect during

the separation process [8]. For this reason, it is necessary to classify by size the soil to be treated before performing gravity concentration. If the density difference between the soil and contaminant particles is significant, the gravity concentration technologies should be particularly suitable for particle separation. The volume capacities of gravity concentrators are 100–500, 25, 4, and 5 t/h for dense media separation (DMS), mineral jig, spiral, shaking table, and MGS-Mozley, respectively [14,16]. The particle size range conditions are reported on Fig. 3.

The most common gravity concentrators, used for soil treatment at large scale, are jigs, shaking tables and spirals (Table 1). Mineral jigs are commonly used to treat coarse sand fractions (800–2000 μm) or gravel fractions (2000–6000 μm) while shaking tables and spirals are more suitable to treat fine to medium/coarse sand fractions (63–2000 μm) (Table 3). Silt/clay (<63 μm) and very fine sand (63–125 μm) fractions can be processed with MGS-Mozley. Bergeron [22] reported the following results for long-term trials in remediation project of brownfield soils from Montreal, Canada: (1) 75% of Cu removal efficiency (823 $\mu\text{g/g}$ of Cu in initial soil) obtained with the use of two jigs (in series) from the 1700–6400 μm fraction; (2) 54% of Cu removal efficiency (1025 $\mu\text{g/g}$ of Cu in initial soil) obtained with the spiral method from the 106–1700 μm fraction; and (3) 47%



DMS= Dense media separation; HIMS= High intensity magnetic separation; LIMS= Low intensity magnetic separation; MGS= Multi gravity separator

Fig. 3. Feed particle size range for application of physical separation techniques. Adapted from [9,14–16,126].

of Cu removal efficiency (924 µg/g of Cu in initial soil) obtained with MGS-Mozley from the <106 µm fraction.

Since Pb is a dense element, gravity concentration may be used for remediation of soils contaminated with particulate forms of Pb (e.g., Pb-based old paint debris, battery-manufacturing/recycling sites, and smelting/mining sites). Density separation with jigs is a well-established method to remove Pb from small arms firing ranges (SAFR) where Pb is mostly present in the form of spent bullets (Table 1, projects #10–13, 15, 16, 20–23, 29, and 30).

3.4. Froth flotation

Froth flotation is a physico-chemical technique that exploits difference of hydrophobic properties to separate metal-bearing particles from the soil matrix. The separation principle is based on the affinity of a particle's hydrophobic surfaces for air bubbles injected in the slurry of soil. The separation process involves three steps: (1) attachment of the desired metal-bearing particles to the air bubbles; (2) the bubbles are gathered in a foam portion; and (3) the foam fraction, which floats up slurry, is removed. The surface of metals-bearing particles is often rendered hydrophobic by the use of a surfactant agent (collector). The froth flotation

is widely used in the mineral industry, and metal sulfides are easier to separate than carbonates and oxides [14]. There are different types of flotation systems including flotation cells and a flotation column.

Froth flotation has been successfully used to remove metals (primarily Cd, Cu, Pb, and Zn) from sediments and soils [24–31]. Some examples of metal removal efficiency obtained with flotation systems are described in Table 3. However, the use of froth flotation as a remediation technique is still less used than other soil washing technologies. Froth flotation appears to be a relevant technique for treating fine-grained matrices, especially anoxic dredged sediments (best separation efficiency in the 20–50 µm range) where heavy metals are mostly present under sulfide forms [25,26].

In soil remediation context, major factors influencing the floatability of metal-bearing particles are: (1) the heterogeneity of the metal compounds; (2) the metal distribution over the different particle size fractions; (3) the presence of high contents of organic matter; and (4) the proportion of the very fine particles <10 µm [26,29]. Since sulfide minerals are more floatable than carbonates or oxides, chemical pre-treatment by sulfidisation has been investigated (Table 3) [24,30]. The efficiency of flotation columns is usually much higher than that of flotation cells

in the finer portion of the grain size range [16,27]. The selective flotation of metal-bearing particles from the particle size fraction $<10\ \mu\text{m}$ is problematic in most mechanical flotation cells because of various phenomena of entrainment and entrapment of the fine hydrophilic undesirable gangue particles [31,32]. The dissolved air flotation (DAF) system, which can produce very small bubbles, is promising to improve the selective flotation for the fine particles range [29]. The conventional flotation systems are less effective in floating large particles ($>200\text{--}300\ \mu\text{m}$) due to the inability of bubbles to carry coarse and heavy particles [14]. Compared to conventional flotation technologies, the separation in froth (SIF) technology is more suitable for separation in the coarser particle size range [14]. Attrition scrubbing is often used prior to the flotation process in order to disaggregate the small particles bound on coarse particles and to remove the coating of a particle's surface. Also, power ultrasound can be used instead of attrition conditioning [33].

In full-scale application, flotation was mostly combined with hydroclassification, and gravity concentration (Table 1). In the 1980s, Dutch companies like Jaartsveld, Mosmans and Heidemij pioneered the flotation technique for soil cleaning with Metso (Swedish company) as a major equipment supplier [34]. The most significant example of full-scale froth flotation use in the US, for metal removal from contaminated soils, is the project performed at King of Prussia Superfund site in 1993 (Table 1, project #3).

3.5. Magnetic separation

Particles present in soil have magnetic susceptibilities which vary from negative (organic), intermediate (paramagnetic minerals and organometallics) to largely positive ferromagnetic minerals [35]. Ferromagnetic material can be attracted by a low intensity magnetic field, while separation of paramagnetic material requires a high intensity magnetic field [18]. Low intensity magnetism separation (LIMS) has been used to recover spent munitions debris at military sites [36] or ferrous/metallic debris material containing high heavy metals concentrations in brownfields [37]. The magnetic separation of heavy metals from the soil matrix is based on the fact that metal contaminants are associated with the ferromagnetic materials. Rikers et al. [35] showed that wet high intensity magnetism separation (WHIMS) is suitable for removing Cr, Cu, Ni, Pb, and Zn from several soils. If the heavy metals are not associated with a ferromagnetic phase, separation is not efficient. When the soil matrix is heterogeneous, as in the case of brownfields, magnetic separation is not significantly efficient to remove metal contaminants from soils [17].

3.6. Electrostatic separation

The use of electrostatic separation for soil remediation appears limited and is rarely used. One example of an electrostatic separation application at full-scale is the PMET's lead-base paint chip separation and recovery technology [38]. This process uses a final step of electrostatic separation after size classification, ferromagnetic separation, and gravity separation steps [39].

3.7. Attrition scrubbing

Typical attrition scrubbers use an intense opposing flow generated by twin impellers in soil slurry with a very high solid content (70–80%) to provide mechanical particle-to-particle scrubbing in order to accomplish two main effects: scouring and breaking [9,40]. The scouring effect involves the removal of coating or film from individual grains. The breaking effect involves the dispersion/separation of silt and clay bonded to sand and gravel particles, and the disintegration of soil agglomerates. Soil scrubbing is accomplished mostly by particle-to-particle attrition, but also by the interaction between the paddles and the particles [41].

Williford et al. [42] showed that preconditioning by attrition scrubbing enhanced size hydroclassification. Marino et al. [43] showed that mechanical attrition increases the removal efficiency of metal on the Wilfley table (gravity concentration). Scrubbing effect produces fresh and clean grain surfaces (by removing oxidized coating), and thus can enhance subsequent froth flotation processes [14]. Attrition scrubbers can also be used to improve the chemical extraction of superficially bound contaminants (adsorbed metal cations) from solid particles [44]. Ko et al. [45] have used a drum-type scrubber (pilot-scale) chemically enhanced by acid leaching to extract metals (As, Ni, and Zn) from soils (Table 1, project #32).

3.8. Integrated process train of physical separation

Table 1 shows that most of the large-scale applications of PS process trains (16 projects reported) primarily exploit the differences in particle size (hydroclassification) and density (gravity concentration). Froth flotation is moderately used. Attrition scrubbing is often employed as a pre-treatment to improve the separation process. Magnetism and electrostatic separators are not often used. In field applications, typical treatment train of physical separation process includes: (1) a preliminary size classification step using mechanical screening to isolate oversized material; (2) a hydroclassification step preceded or followed by attrition scrubbing to provide suitable particle size range for further treatments; (3) the treatment of the sand fraction by gravity concentration or froth flotation; (4) the treatment of the fine fraction; and (5) the management of the generated residuals.

Many physical separation processes were based on simple particle size separation because the fine fraction (clay and silt) is often considered as contaminated and the coarse fraction (sand) is considered as uncontaminated. However, metal contamination can be distributed throughout the various particle size fractions of soils and concentrations can be high in sand fraction, especially for urban or industrial soils polluted by heterogeneous waste disposal [46–48]. If metal contamination is of particulate nature and is abundant in all particle size fractions, separation only based on size cannot accomplish a sufficient separation of metal contaminants. In this case, the separation based on density or floatability must be investigated. The physical separation treatment train can require crushing, desliming, dewatering, and water treatment. Physical separation can be used as a stand-alone volume reduction process or as pre-treatment prior to metal

recovery (Table 1). In certain cases, Pb and Hg may be recovered under a saleable form. In remediation projects of shooting range soil, the Pb concentrates were usually sent to smelter for metal recycling (Table 1).

3.9. Advantages/disadvantages of physical separation technologies

This section provides general comments for the integrated processes, specially large-scale applications. The advantages and disadvantages for each technology type were specifically discussed in the preceding paragraphs. Physical separation presents many advantages: (1) this technology can treat both organic and metal contaminants in the same treatment system; (2) the volume of soil to be further treated (for metal recovery) or to be disposed of off-site are considerably reduced; (3) the soil processed can be returned to the site at low cost; (4) the metal recovered may be recycled in certain cases (e.g., sent to smelting facility); (5) the treatment train systems are easily modular and some mobile unit systems are available at full-scale for on site remediation; and (6) the technologies are well established in the mineral processing industry and the operational costs are usually low.

On the large-scale applications, the soil treatment by physical separation presents some disadvantages: (1) this treatment system requires a large equipments and large spaces for soil treatment; (2) the volume of soils to be treated must be large to be cost effective (>5000 t for treatment on site); (3) wash-water treatment and off-site disposal of residual solids may be required, thus significantly increases the cost [8,20].

4. Chemical extraction technologies

Chemical extraction uses an extracting fluid containing a chemical reagent (acids/bases, surfactants, chelating agents, salts, or redox agent) to transfer the metals from the soils into an aqueous solution. In extractive metallurgy, the chemical extraction procedures, referred to by the term “hydrometallurgy”, are extensively employed for recovery of the metals from ores, concentrates, and recycled or residual materials [49]. In the soil remediation context, solubility enhancement can be accomplished by leaching solutions in which the metal contaminants are dissolved; or by converting the metal compounds into forms that are more soluble (e.g., conversion to soluble metal salts by valence change). In this review, the use of five leaching solution types will be separately discussed: (1) acids; (2) salts and high-concentration chloride solutions; (3) chelating agents; (4) surfactants; and (5) reducing or oxidizing (redox) agents.

Table 4 summarizes the soil types, the treated metals (initial concentrations), the leaching methods, the studied factors in leaching process, the overall results and conclusions of 24 laboratory investigations (18 studies involved EDTA; three studies compared EDTA vs. other chelating agents; seven studies compared EDTA vs. acids; six studies involved the chloride salt solutions, four studies compared several acids). Generally, acids rely on ion exchange and dissolution of soil components/discrete metal compounds to extract metals.

The use of high-concentrations chloride salt solutions at low pH conditions combines the acid leaching action and the formation of metal chloro-complexes to extract metals from soils. Chelating agents solubilize metals through complexation. Surfactants target desorption of metals from soil interface. The redox manipulation aims to enhance metal solubilization through a valence change. The choice of the extracting reagent depends on the metal type, metal concentration, metal fractionation/speciation, and soil characteristics (Table 4). Strong acids such as hydrochloric acid (HCl) and chelating agents such as ethylenediaminetetraacetic acid (EDTA) are commonly investigated to extract heavy metals from soils.

4.1. Applicability and limitations of chemical extraction

Metal removal efficiency by the chemical extraction process depends on the soil geochemistry (e.g., soil texture, cation exchange capacity, buffering capacity, and organic matter content); metal contamination characteristics (type, concentration, fractionation, and speciation of metals); dosage and chemistry of extracting agent; and processing conditions (solution pH, residence time, number of successive extraction steps, mode of reagent addition, liquid/solid ratio, etc.) (Table 4). Several experimental results of metal removal efficiency according to the leaching methods, the reagent types (EDTA, HCl, and salts solutions) and the soil characteristics are reported in Table 5.

The speciation (distribution of chemical species) and fractionation (fractions according to bonding with specific soil substrates) of metals in soils are important parameters for determining the metal removal efficiency by chemical treatment. The metal speciation analysis can be complicated (especially when the soil is contaminated with a complex mixture of metal compounds) and the metal fractionation according to soil substrates is often applied. The partitioning of metals according to their association with the soil substrates is usually determined by the sequential extraction procedure [47,48]. The analytical protocols used generally involve five fractions: (F1) exchangeable, (F2) acid soluble/carbonate bound; (F3) reducible/Fe–Mn bound; (F4) oxidizable/organic matter and sulfide bound; (F5) residual [50] (Table 4). Van Benschoten et al. [51] have studied metal partitioning for up to 10 fractions.

The fractions most amenable to metal removal by chemical leaching are: (1) exchangeable; (2) associated with carbonates; and (3) associated with reducible Fe–Mn oxides of soils [52] (Table 4). However, extraction of metal bound to exchangeable and carbonate fractions was faster compared to extraction of metal bound to Fe–Mn oxides [53,54]. In describing leaching with EDTA and HCl, Van Benschoten et al. [51] reported that non-detrital Pb (i.e., associated with water soluble, carbonates and organic) was removed from soils, while Pb bound to the Fe-oxides, sulfide and residual fractions was not removed. Organically bound metals can be extracted along with the target organic contaminants by the solvent extraction method [4]. The removal efficiency of metals from the distinct fractions depends on the extracting reagents used (Table 4). For instance, due to dissolution effects, certain acid leaching processes may partially remove metals from the crystalline lattice [55]. Nevertheless, the metal

Table 4
Laboratory investigations of chemical extraction technologies

Soil type	Metals ($\mu\text{g/g}$)	Leaching method	Reagent	Studied factors in leaching process	Overall results and conclusions	Leachate treatment	Ref.
Calcareous soils polluted by mining and smelting activities in Lavrion, Greece	Cd (20–130) Pb (500–34,800) Zn (700–20,200)	Batch	EDTA	Test with seven different soil samples; successive steps (1–2) with $\text{Na}_4\text{-EDTA}$ vs. $\text{Na}_2\text{-EDTA}$; EDTA dosage (0.2–1 M), i.e., $\text{EDTA}/\sum\text{Me}$ molar ratio (1–23); S/L (10–36%); study of EDTA/Ca vs. EDTA/Me molar ratio	Pb RE varied for the different samples (50–98%). Cd and Zn RE was <50%. Best results were obtained with two steps, high conc. of $\text{Na}_2\text{-EDTA}$ (0.25 M, i.e., $\text{EDTA}/\sum\text{Me}$ molar ratio was >20) and low S/L ratio (10%). EDTA may contribute to the co-dissolution of CaCO_3	–	[65]
Calcareous soil from the battery site, Canada	Pb (24,600) Cd (27) Zn (241) Cu (43) Ni (120)	Batch	EDTA	EDTA dosage (0–0.2 M); pH (4–8); extraction kinetic; extraction mechanism (two-reaction models); MF (6 fractions)	Removal of Cu/Cd/Ni/Zn was less effective than removal of Pb. RE of Pb was 99% with high EDTA dosage (0.2 M) and within 12 h of the leaching. Extraction of Pb bound to carbonates and exchangeable fractions was faster compared to extraction of Pb bound to oxides	Nano-filtration for Pb-EDTA complex recovery (98%) ^a	[54]
Artificially contaminated sandy soil	Cu (1230)	Batch	EDTA	EDTA/Cu molar ratio (1–12.5); L/S ratio (5–25); pH (4.8–6.56); extraction time (0–25 h); extraction mechanism of Ca^{2+} , Fe^{3+} and Cu^{2+}	Cu RE = 80–90% within 5 h of the leaching. Cu RE strongly depended on L/S ratio and EDTA/Cu ratio. Best results were obtained with L/S = 12.5 and EDTA/Cu = 12.5	–	[64]
Four soils from mining and smelting site in Slovenia	Pb (1136–4424) Zn (288–5489)	Batch/heap	EDTA	EDTA dosage (0.00375–0.06 M); pH (4.5–9); Successive steps (1–10); interference of major cations (Ca, Fe) with Pb/Zn-EDTA complexation; laboratory simulation of soil heap leaching (time = 0–72 h)	Increasing EDTA conc. did not produce a proportional gain in RE. Multi-steps using low EDTA dosage gave best results compared to single-step mode. Fe^{3+} interfered more strongly with Pb/Zn EDTA-complexation when single step mode was used. The interference of Ca^{2+} was less important	–	[63]
Soil from Pb-smelting site in Mezica Valley, Slovenia	Pb (1243) Zn (1190)	Batch/heap	EDTA	Small-scale heap leaching; Successive steps (1–6) with EDTA/Pb molar ratio (0.42–6.67) and EDTA/Zn molar ratio (0.14–2.2); extraction time (0–96 h); MF study (six fractions)	Multi-step using low EDTA dosage gave best results compared to single-step mode. EDTA extracted more Pb than Zn (Zn bound to the residual soil fraction)	Degradation of EDTA by ozone/UV treatment and absorption of metals	[78]

Four soils (mining activity) in UK and France	Cd (49–380) Cu (42–1350) Pb (265–9430) Zn (1920–30,260)	Batch/column	EDTA	(1) Batch tests (L/S = 5): EDTA dosage (0.01 M); EDTA/ \sum Me ratio for initial/final soil; (2) column tests: effect of the mode of EDTA addition (continuous and pulse mode); EDTA dosage (0.01–0.025 M); (3) MF study (five fractions) before and after treatment	(1) Batch tests: EDTA extracted the metals similarly. (2) column tests: EDTA extracted the metals differently. The results showed that metal removal occurs differently in batch and column leaching	–	[56]
Artificially contaminated soil	Pb (1399) Zn (752)	Batch	EDTA	Extraction time (0.5–4 h); EDTA/Pb ratio and EDTA/Zn ratio (1–2); pH (5–9); Initial Pb and Zn conc. in soil; study of competition between Zn and Pb	Optimal conditions for EDTA leaching were: extraction time = 2 h; EDTA/Pb ratio = 2 and pH 7 for Pb; EDTA/Zn ratio = 1 and pH 9 for Zn. Metals RE increased with an increase of initial metals conc. (with a fixed EDTA/Me ratio). There is competition between Zn and Pb under different EDTA dosage. Pb RE was higher than Zn RE with low EDTA dosage	–	[77]
Artificially contaminated soil	Cd (269) Pb (2510) Ni (605)	Batch	EDTA	L/S ratio = 20; EDTA dosage (0.001–0.01 M), i.e., EDTA/ \sum Me ratio (0.8–8); pH (4.7–8); extraction times (15–240 min); tests with fresh EDTA and recycled EDTA; MF study (five fractions)	Optimum condition for metals RE depends on soil geochemistry and MF. The order of RE was Cd > Pb > Ni. EDTA appeared capable for extracting the Cd/Pb/Ni bound to the exchangeable, acid soluble, reducible and part of the oxidizable fractions	EDTA regeneration (84%) and metal phosphates precipitation (89–95%) ^a	[73]
Soil contaminated by metals and PCB in Montreal, Canada	Cd (56) Cr (436) Cu (2726) Ni (364) Pb (17,944) Zn (8940)	Batch	EDTA + surfact.	Tests with EDTA (0.002 M), EDTA + surfactant (anionic and non-anionic) with various ultrasonication times (3, 5, 10, 30 min); tests with fresh and recycled EDTA. Study of Fe, Mg, and Fe removal	The use of surfactants improved EDTA leaching. RE with EDTA + surfactant (non-anionic) was effective for Pb (73%) and moderately effective for Cu (49%), Cd (36%) and Zn (44%). RE was ineffective for Cr and Ni (mainly associated with residual soil fraction)	EDTA regeneration and metal precipitation by addition of Ca(OH) ₂ and Mg ⁰ (73–96%) ^a	[76]
Artificially contaminated soil	Cd (603) Cr (1231) Pb (742) Zn (624)	Batch/column	EDTA + red.	(1) Batch tests: EDTA (0.01 and 0.1 M) and/or reducing agent Na ₂ S ₂ O ₅ (0.1 M); L/S ratio (5,12.5,25); pH (3.9–6.3); extraction time (2–90 h); (2) column tests: EDTA (0.01 M) and/or Na ₂ S ₂ O ₅ (0.1 M)	RE depended on the dissolution of metal–mineral bond, and the dispersion of metal in the washing solution. RE of Cr was low compared to RE of Cd, Pb, Zn. The use of reducing agent improved the EDTA leaching. L/S ratio had less effect. Column tests resulted better metal RE rather than batch tests	–	[11]

Table 4 (Continued)

Soil type	Metals ($\mu\text{g/g}$)	Leaching method	Reagent	Studied factors in leaching process	Overall results and conclusions	Leachate treatment	Ref.
Two metal-polluted soils from Indianapolis, IN and Palmerton, PA	Cd (197–280) Pb (812–210,000) Zn (521–2700)	Batch	EDTA Oxalate	EDTA (1 M) vs. oxalate (1 M) (time = 24 h); pH (3–10); study of Fe-oxides removal; MF (five fractions)	MF was a major factor. EDTA was efficient to extract metal associated with non-detrital and organic fractions. EDTA was less efficient to extract metals bound to oxide fraction. Oxalate was efficient to extract metals associated with oxide fraction	–	[53]
Two urban soils in Montreal, Canada	Cd (1–6) Cu (130–700) Pb (269–800) Zn (360–2650)	Batch	EDTA HCl	HCl (0.001 M) vs. EDTA (0.00274 M) (time = 24 h); successive steps (1–12) with EDTA; EDTA dosage (0.00684–0.0274 M); pH (4 and 8.5)	Acid washing with low HCl conc. was ineffective because the soils had high buffering capacity. EDTA was more effective. RE depended on EDTA dosage (best result with high conc.). High silt/clay content affected metal RE	Anion exchange resin for EDTA–metal complex recovery (90–99%) ^a	[60]
Artificially contaminated soil	Pb (5000)	Column	EDTA HNO ₃	Tests with 10 Pb-compounds (adsorbed Pb ²⁺ , carbonate, sulfate, oxide, dioxide, sulfide, elemental forms of Pb, Pb-compound from paint); tests with HNO ₃ at various pH (1–6); tests with EDTA (0.0003 and 0.001 M, i.e., EDTA/Pb ratio = 1 and 3) at pH 6	Best results of acid leaching is obtained at pH 2. RE of adsorbed, carbonate, sulfate, oxide forms was effective and RE of sulfide, dioxide, Pb from paint, and elemental forms was ineffective. RE with EDTA (EDTA/Pb ratio = 3) was effective for adsorbed, carbonate, sulfate, oxide, dioxide forms, while was ineffective for other tested forms of Pb	–	[12]
Seven Pb-contaminated sandy soils in the US	Pb (1394–11,933)	Batch	EDTA HCL HCLO ₄ H ₂ SO ₄ Red.	Acids vs. EDTA (0.01 M) at pH (1,2,3); temperature (25, 50 °C); L/S ratio (5, 10, 20); the use of reducing agent NH ₂ OH–HCl (0.4 M); extraction kinetic; MF study (10 fractions)	HCl was effective for Pb RE at low pH. RE and kinetic mainly depended on pH. The use of EDTA (0.1 M) improved Pb RE at pH 3 and not at pH 1. L/S ratio and temperature had less effect. Pb not removed by acids/EDTA leaching was associated with Fe-oxides, sulfide and residual. The use of reducing agent improved removal of Pb bound to Fe-oxides	–	[51]

Soil polluted by battery recycling and Pb-smelting operation, IN	Pb (65,200)	Batch	EDTA ADA PDA HCL	HCl (0.1–1 M) vs. chelatants (0.0225–0.075 M); extraction time (1–5 h); successive steps (1–3); MF study (five fractions)	The order of Pb RE: EDTA > ADA > PDA > HCl. The order of Cd RE: HCl > ADA ≈ PDA ≈ EDTA. RE depended on EDTA dosage. Three-step leaching (1 h) improved RE. Cd was removed from the crystalline lattice by HCl leaching	Metal hydroxides precipitation by addition of Ca ²⁺ and NaOH (72–93%) ^a	[55]
Soil polluted with slags and sulfur compounds in Lavrion, Greece	As (7540) Cu (4100) Pb (64,195) Zn (5590)	Batch	EDTA HCl HNO ₃ H ₂ SO ₄	Tests with HCl (1, 2, 3, 6 M), H ₂ SO ₄ (6 M), HNO ₃ (6 M), Na ₂ -EDTA (0.1 M); study of extraction kinetic for HCl (1 M) and Na ₂ -EDTA (0.1 M) leaching; mineral analysis by XRD of metal compounds	RE highly depended on the metal forms. HCl resulted best RE compared to other acids. RE was improved with increasing HCL dosage and at long extraction time (4 h). EDTA was more effective at low leaching time (<1 h). HCl 1 M (4 h leaching) presented better RE compared to EDTA 0.1 M (1 h leaching). HCL 1 M strongly affected soil matrix. RE of As was ineffective with EDTA	–	[67]
Artificially contaminated soil	Cd (49) Pb (294) Cr (270)	Batch	EDTA NTA DTPA HNO ₃ CaCl ₂	Single-step at pH 7; extraction time (15–300 min); tests with EDTA/NTA/DTPA (0.001–0.01 M); comparison of EDTA/NTA/DTPA (0.005 M), HNO ₃ (pH 2–3), and CaCl ₂ (0.5 M); MF study (five fractions)	The order of Pb RE: EDTA ≈ NTA ≈ DTPA > HNO ₃ > CaCl ₂ . The order of Cd RE: EDTA > NTA > DTPA > HNO ₃ > CaCl ₂ . Chelating agents were ineffective in removing Cr (mainly associated with oxidizable and residual fraction)	–	[74]
Soil from mining area located in Korea	As (41) Ni (88) Zn (335)	Batch	HCl H ₃ PO ₄ H ₂ SO ₄	Tests with HCl, H ₃ PO ₄ , H ₂ SO ₄ at pH 2–3; study of RE vs. particle size fractions (0.841–2, 0.420–0.250, <0.074 mm); extraction time (10 to 25 min) and MF (four fractions)	Acids with oxyanions (H ₃ PO ₄ , H ₂ SO ₄) was effective for removing As and Zn. HCl was less effective in As removal. Acid leaching of Ni was less efficient (residual fraction). Acid leaching caused a loss of OM (50%) and an increase of acidity (7.6–3.3) of the treated soil	–	[57]
Two contaminated rice soils in Taiwan	Cd (4) Cr (720) Cu (800) Ni (850) Pb (1849) Zn (1222)	Batch	HCl + CaCl ₂	Study of the relation of soil suspension pH with the amount of H ⁺ added and the loss of H ⁺ from solution; Study of the dissolution of Fe and Al oxides by HCl; Effect of CaCl ₂ dosage (0–0.1 M) and HCl dosage (0.001–0.01 M) in RE of Cd with HCL + CaCl ₂ solution at various pH (1–7)	The use of CaCl ₂ increased RE in diluted HCl (<0.01 M) for Cd removal. Fe–Al oxides are attacked by HCl with dosage >0.01 M	–	[66]

Table 4 (Continued)

Soil type	Metals ($\mu\text{g/g}$)	Leaching method	Reagent	Studied factors in leaching process	Overall results and conclusions	Leachate treatment	Ref.
Three artificially contaminated soils	Pb (995–1078)	Batch	HCl + CaCl_2	Three soil types: kaolinitic, smectitic and allophonic soil; successive steps (1–10) using HCl (1 M) followed by CaCl_2 (0.1 M) washing; study of Pb bioaccessibility after the soil washing; MF study (three fractions)	The successive batch washing with HCl (1 M) + CaCl_2 (0.1 M) was effective in removing Pb. RE depended on soil properties (buffering capacity, CEC, humic substance content, and clay mineral content)	–	[62]
Two soils from abandoned Pb-battery recycling sites, TX and FA	Pb (14,400–67,400)	Batch	NaCl HCl EDTA	Tests with seven chloride solution types NaCl, CaCl_2 , HCl, MgCl_2 , NH_4Cl , KCl, LiCl ($\text{Cl}^- = 4.3 \text{ M}$); successive steps (1–6, time = 30 min) using HCl (0.3 M) + NaCl (4.3 M); L/S ratio (5–50); tests with HCl (0.2 M) + NaCl (4.3 M) vs. EDTA (EDTA/Pb ratio: 4.6–40) and pH (2–10); tests with HCl (0.1–4.3 M) vs. acidified NaCl (4.3 M) solutions; mineral analysis (Pb species) by XRD; kinetic and mechanism extraction	Best results (RE = 97%) were obtained with successive two-step extraction (L/S = 7, time = 1 h) using acidified (pH 4) NaCl solution (4.3 M to saturated 6 M). Kinetic study suggested that Pb removal mechanism is composed of three stages: (1) extraction of free-Pb precipitates (quick process: <1 min); (2) cation exchange of Pb located on soil surface (30 s to 5 min); (3) removal of Pb located within soil structure (slow process Pb after 5 min)	–	[69]
Soil from Pointe-aux-Lievres, Canada	Pb (2730)	Batch	NaCl + HCl	NaCl dosage (0–6 M); pH (2–4); soil pulp density (5–30%); extraction times (0–1 h)	Pb RE (65–75%) was more effective with high Cl^- conc. (5.5 M), pH 2 and at 30% soil pulp density. Pb RE was independent of acid type, but depended on the pH (best result at low pH)	Electrochemical reduction/coagulation for Pb recovery (95%) ^a	[123]
Calcereous soil from the battery site in St-Jean-sur-Richelieu, Canada	Pb (2730)	Batch	NaCl + HCl	NaCl (8 M); successive steps (1–6); study of Ca removal; extraction kinetic; MF study (five fractions)	Six steps with NaCl (8 M) was effective (RE = 93%); RE increases with extraction time (RE > 80% after 90 h). Extraction appeared to be controlled by a first-order rate (Pb extraction from carbonate and exchangeable soil fractions)	Regeneration of Cl^- and metal precipitation with addition of NaCO_3 , CaCO_3 ; or lime (90–98%) ^a	[71]
Fine-grained soil from Montevecchio, Italy	Cd (34) Zn (3600) Pb (16,000)	Column/pile	HCl + CaCl_2	Column tests: three successive steps with HCl (0.2 M) + CaCl_2 (1.9 M) at pH < 0.5 followed by seven successive steps with CaCl_2 (2 M) at pH 6.5. Study of Mn, Fe, Al, Mg removal; particle size distribution vs. metal concentration before and after treatment	Chloride solution with CaCl_2 + HCl was effective in metal removing from soil (poor in calcite). The treated soil matrix was sensibly unaffected (total weight loss = 3.5%; initial pH 5.6; final pH 5.15)	Regeneration of Cl^- and metal precipitation with CaCl_2 at pH 9–12 (70–94%) ^b	[61]

EDTA: ethylenediaminetetraacetic acid; ADA: *N*-2-acetamidoiminodiacetic acid; PDA: pyridine-2,6-dicarboxylic acid; NTA: nitrilotriacetic acid; DTPA: diethylenetriaminepentaacetic acid; M: mol/L; RE: removal efficiency; L/S: liquid/solid; MF: metal fractionation; Surf.: surfactants; Red.: reducing agent; $\sum \text{Me}$: molar sum of metals; OM: organic matter; CEC: cation exchange capacity.

^a Removal efficiency of the dissolved metals from the leaching solution (varies according to the metal types or the processing conditions).

^b Removal efficiency for the whole process (leaching + precipitation).

Table 5
Examples of experimental results in metal removal efficiency according to the leaching method and the soil characteristics

Leaching method	Reagents (mol/L)	Soil description	Soil pH	CEC ^a (cmol/kg)	Texture ^b S/S/C (%)	OM ^c (%)	Ca (%)	Metal	Conc. (µg/g)	RE ^d (%)	Ref.
Batch 1 h, 3 steps, pH 4.5 (chelation)	EDTA (0.0225)	Soil contaminated by smelting and battery recycling operations	7.4	14.3	68/17/15	8.2	–	Pb	65,200	56	[55]
								Cd	52	37	
Batch 24 h, 12 steps, pH 7–8 (chelation)	EDTA (0.00275)	Urban soil contaminated by industrial activity	8.03	12.8	69/24/7	2.8 ^e	18	Cd	6.3	53	[60]
								Cu	700	49	
								Pb	800	76	
								Zn	2,650	84	
Batch 1 h, 1 step, pH 6 (chelation)	EDTA (0.1)	Soil contaminated with slags and metallurgical wastes	7.0	–	–	–	6.2	As	7,540	13	[67]
								Cu	4,100	41	
								Pb	64,195	44	
								Zn	55,900	38	
								As	1,200	8	
Batch 22 h, 2 steps (chelation)	EDTA (0.25)	Calcareous soil (S1) contaminated by mining and smelting activities	8.3	–	42% <63 µm	–	11.6	Cd	100	37	[65]
								Pb	32,000	71	
								Zn	15,000	49	
								As	1,200	8	
								Pb	67,400	>97	
Batch 1 h, 2 steps, pH 4 (acid leaching + Cl ⁻ complexation)	HCl + NaCl (4.3)	Soil from battery recycling site	7.0	9.5	51/36/13	3 ^e	30	Pb	67,400	>97	[69]
Batch 1 h, 1 step, pH 4 (acid leaching + Cl ⁻ complexation)	HCl + NaCl (5.5)	Fine-grained fraction of industrial soil	–	–	100% <20 µm	–	5.7	Pb	2,730	65	[123]
Column: three steps with HCl (0.2 M) + CaCl ₂ (1.9 M) at pH < 1 followed by 7 steps with CaCl ₂ (2 M) at pH 6.5 (acid leaching + Cl ⁻ complexation + ion exchange with Ca ²⁺)	HCL + CaCl ₂	Fine-grained soil contaminated by mining activities	5.6	–	43/29/28 ^f	–	0.7	Cd	34	75–80	[61]
								Zn	3,600	75–80	
								Pb	16,000	90–95	
Batch 1 h, three steps, pH 4.5 (acid leaching)	HCL (1)	Soil contaminated by smelting and battery recycling operations	7.4	14.3	68/17/15	8.2	–	Pb	65,200	35	[55]
								Cd	52	56	
Batch 1 h, one step, pH 4 (acid leaching)	HCl (2)	Soil contaminated with slags and metallurgical wastes	7.0	–	–	–	6.2	As	7,540	92	[67]
								Cu	4,100	42	
								Pb	64,195	57	
								Zn	55,900	67	

^a Cation exchange capacity.

^b Sand/silt/clay.

^c Organic matter content.

^d Removal efficiency.

^e Organic carbon content (%).

^f The soil was agglomerated before the soil leaching treatment.

fractionation data does not always clearly explain metal removal efficiency because removal efficiency also depends on other factors such as metal concentration and soil geochemistry [56].

In addition, removal efficiency depends on the metal type to be extracted and the valence of the element. Generally, the extractability of most cationic heavy metals (e.g., Cd, Cu, Pb, and Zn) increases when the solution pH decreases. Indeed, at low pH, adsorption onto soil of the cationic heavy metals decreases and the dissolution of metal compounds increases. On the other hand, the solubility of oxyanions of the metalloid As increases when the solution pH increases [57]. In addition, the adsorption of chromium Cr(VI) anionic species is enhanced at low pH [58]. Hence, the simultaneous treatment of both anionic and cationic metal species that have dissimilar chemical behavior in aqueous solution, can be ineffective. Furthermore, Isoyama and Wada [58] reported that HCl leaching was relatively efficient for chromate (CrO_4^{2-}) removal from non-allophanic soils but it was inefficient for removal of trivalent chromium Cr^{3+} , particularly from soils having high cation exchange capacity (CEC) and organic matter content (due to complexation by humic substance and adsorption via cation exchange reactions).

If metal is not under an adsorbed form, the removal efficiency depends on solubility of metal compounds in the washing fluid, which are governed by the solubility product ($K_{s.p.}$) values. The treatment of particulate forms of metals is more difficult to achieve compared to the adsorbed ionic forms [59].

Factors that may limit the applicability and effectiveness of the chemical process include: (1) high clay/silt content; (2) high humic content; (3) high content of Fe and Ca element; (4) high calcite content or high buffering capacity; (5) simultaneous contamination of both cationic or anionic heavy metals; (6) high heterogeneity of soil; and (7) metals associated with residual soil fraction, imbedded in the mineral lattices, or discrete particle forms. The fine-grained soils may require longer contact times and may reduce chemical extraction efficiency [60,61]. Nevertheless, Table 5 reports several leaching processes that have treated soils having a high clay/silt content (>50%). High humic content can inhibit metal extraction because COOH groups (adsorption sites) on humic substances have high affinity for heavy metals [62]. The corresponding cations of major element Fe and Ca may interfere with chelating process [63–65]. High calcite content or high buffering capacity may decrease the acid leaching efficiency [60]. High heterogeneity of soils can affect formulations of extracting fluid and may require multiple process steps.

4.2. Acid extraction

Acid extraction is a proven technology to treat soils, sediments, and sludges contaminated by metals and commercial-scale units are in operation [4]. The pH of the washing fluid plays a significant role in the extractability of heavy metals from soils. Several mechanisms contribute to the extraction of metals from soil using an acid solution: (1) desorption of metal cations via ion exchange; (2) dissolution of metal compounds; and (3) dissolution of soil mineral components (e.g., Fe–Mn oxides) which may contain metal contaminants [61,66]. At low pH, the protons

(H^+) added can react with soil surface sites (layer silicate minerals and/or surface functional groups including, e.g., Al-OH, Fe-OH, and COOH groups) and enhance desorption of metal cations, which are transferred into the washing fluid [62]. Kuo et al. [66] showed that acid leaching with 0.1 M HCl contributes to a significant dissolution of Fe and Al oxide surfaces, and phyllosilicates. At $\text{pH} < 2$, this dissolution process replaces ion exchange in metal extraction [66].

Acid leaching may involve strong mineral acid such as hydrochloric (HCl), sulfuric (H_2SO_4), nitric (HNO_3), phosphoric (H_3PO_4) or weak organic acid such as acetic acid. While, acetic acid has been used in field demonstrations at Fort Polk in Leesville, LO (Table 1, project #23), the nuisance of odors and its relative low strength limits its efficiency [21]. The removal efficiency of different mineral acid types strongly depends on the metal type, the soil geochemistry, and the reagent concentrations (Table 4). Moutsatsou et al. [67] showed that the extraction of metals (As, Cu, Pb, and Zn) from soils, highly contaminated by metallurgical materials, was more effective with HCl compared to H_2SO_4 and HNO_3 . On the other hand, Ko et al. [45] showed that: (1) the extraction of Zn and Ni (cationic) was similar in the use of HCl, H_2SO_4 and H_3PO_4 ; (2) the extraction rate of As (anionic) was higher for the use of H_2SO_4 and H_3PO_4 compared to HCl. Unlike HCl, the use of H_2SO_4 or H_3PO_4 acids, which involve competitive oxyanions (PO_4^{3-} or SO_4^{2-}), may decrease the re-adsorption of As anionic species on reactive surfaces of soil [57].

Many experimental and field test results have shown the efficiency of the HCl leaching process for extracting heavy metals from non-calcareous soils. HCl is often used for chemical leaching at full-scale (Table 1). The co-dissolution of soil components by acid leaching is a critical parameter from an environmental and an economic point of view. Acid leaching strongly affects soil structure and causes important losses (up to 50%) of the soil mineral substances [61] and organic matter [57]. Co-dissolution of the soil matrix increases the consumption of acid reagent and the complexity of the wastewater treatment [61]. Furthermore, acid leaching causes a high increase in acidity of the treated soil [57]. Acid leaching may be ineffective for soils that have a high buffering capacity such as calcareous soils [60]. Although acid leaching is efficient in extracting metals from the soils, its large-scale application has numerous disadvantages: (1) strong acids may destroy the basic nature and the soil structure, thus affecting soil microbiology and fertility; (2) wastewater and processed soils need to be neutralized; (3) neutralization of wastewater creates enormous amount of new toxic residues; (4) disposal of solid/liquid residues and processed soil may be problematic; and (5) cost markedly increases with wastewater processing and soil neutralization.

4.3. Salt solutions and high-concentration chloride solutions

The use of diluted acid solutions containing chloride salts (such as CaCl_2) may be an effective alternative to the acid leaching at high concentrations. The processed soil is practically unaffected by the saline leaching with diluted acid. Indeed, the

co-dissolution of the soil matrix is less significant and the pH of the final soil is not significantly lower compared to initial soil [61]. Kuo et al. [66] reported that the removal efficiency of Cd from rice soils with a 0.001 M HCl and 0.1 M NaCl₂ solution was similar to the removal efficiency obtained with the acid leaching using a 0.01 M HCl solution. The increase in the removal of cationic metals (such as Pb²⁺ and Cd²⁺) with CaCl₂ addition in the acid leaching results from two processes: (1) ion exchange of Ca²⁺ with Pb²⁺/Cd²⁺ on the reactive surface sites of soil matrix; (2) formation of stable and soluble metal chloro-complexes with chloride ions Cl⁻ (e.g., Cd²⁺ + yCl⁻ ⇌ CdCl_y^{2-y}) [61,66]. Isoyama and Wada [62] reported that a second washing step with 0.1 M CaCl₂ (after a 1 M HCl leaching step) was used to prevent a re-adsorption of the extracted Pb on cation exchange sites of silicate layer minerals having a permanent negative charge. The destruction of a soil's physico-chemistry and microbiology is minimized by using successive leaching steps with a solution of CaCl₂ at low concentrations (0.1 M) and slightly acidified [66,68].

Several researchers investigated the use of chloride salt solutions at high concentrations (>1 M) and acidic conditions for removing high Pb concentrations from soils (Table 4). The chloride ions Cl⁻ at high concentrations form soluble chloro-complexes with Pb²⁺ such as PbCl₃⁻ and PbCl₄²⁻ [69]. However, Eh and pH parameters must be monitored for obtaining the optimum thermodynamic conditions and preventing the formation of an insoluble compound PbCl₂ [70]. In high ionic strength solutions, the sodium cation Na⁺ (of the concentrated NaCl solutions) may play a significant role in Pb extraction via ion exchange [69]. The acidified NaCl solutions were more efficient (or comparable) than conventional extractants (EDTA and HCl) for removing Pb from clayey or fine-grained soils (Table 5).

Unlike the leaching with concentrated HCl, the concentrated NaCl solution is effective in removing Pb from calcareous soils without a high Ca extraction [71]. The leaching with an acidified 2 M NaCl solution (enhanced with an oxidant agent) has been tested at pilot-scale for the remediation of highly Pb-contaminated soils (Table 1, projects #29 and 30). The free chloride ions are often recycled and the extracted metals are recovered by: (1) chemical precipitation with addition of sulfide, hydroxide, carbonate compounds or (2) electrochemical coagulation/reduction (Table 4). Meunier et al. [72] showed that the electrochemical coagulation treatment was more effective than chemical precipitation for removing the dissolved metals from acidic and saline leachate; however its cost is higher.

4.4. Chelant extraction

Since chelating agents have the ability to form stable metal complexes, their use offers a promising approach for the extraction of metals from contaminated soils. There are five major factors in the selection of chelating agents for metal extraction from soils: (1) chelating agents should be able to form highly stable complexes over a wide pH range; (2) the metal complexes that are formed should be nonadsorbable on soil surfaces; (3) the chelating agents should have a low biodegradability if the reagents is to be recycled for reuse in the process; (4) the

reagents used should be cost effective; (5) metal recovery should be cost effective [11,52,56,63]. The main advantage of the use of chelating agent (such as EDTA) compared to strong acids (such as HCl) is that chelating agents cause less destruction of the soil structure. However, EDTA presents two main disadvantages compared to HCl: (1) the chemical products are more expensive; (2) EDTA may pose a serious ecological threat if it is not recycled or destroyed in the washing process because EDTA has a low biodegradability degree (resistant to chemical and biological degradation) and has the potential for remobilizing heavy metals in the environment [73,74].

Many chelating agents have been tested and compared (Table 4). Peters [52] showed that EDTA, nitrilotriacetic acid (NTA) and acid citric were effective, while other chelating agents such as gluconate, oxalate, Citranox, and ammonium acetate were ineffective in removing Cu, Pb, and Zn from Aberdeen Proving Ground soils. Carboxylic acids such as EDTA and NTA are chelating agents hydrolytically stable at high temperature and pH levels [75]. However, NTA is not recommended for use in soil remediation because it is hazardous for human health [74]. Moreover, EDTA forms more stable complexes with most of the heavy metals when compared to NTA [75].

EDTA is recognized as the most effective synthetic chelating agent to remove heavy metal (especially Pb, Cd, Cu, and Zn) from soils because of: (1) EDTA has a strong chelating ability for cationic heavy metals; (2) EDTA leaching process can treat a broad range of soil types; and (3) EDTA is recoverable and reusable (low biodegradability degree) [56,64,73,76]. The EDTA leaching process has been well demonstrated through many laboratory studies to extract metal cations bound on soil particles (Table 4). On the other hand, EDTA appears ineffective for extracting anionic metal As (Table 5).

Metal removal efficiency with EDTA highly depends on soil characteristics and metal fractionation (Table 6). In general, EDTA is effective in removing metal cations bound to exchangeable, carbonate and organic fraction, while EDTA is less efficient in extracting metals bounds to reducible/Fe–Mn oxide fraction [11,54,65]. Elliott and Shastri [53] have demonstrated that oxalate was more effective than EDTA to remove the metals associated with Fe–Mn oxides of soil (attacks the hydrous oxides). The metals bound to residual fraction are not extracted by EDTA (Table 6). Unlike acid leaching (low concentration), the EDTA complexing process may be efficient in treating calcareous soils [54,60]. However, EDTA may contribute to the co-dissolution of calcite, thus reducing removal efficiency of metals [65].

The low selectivity of EDTA causes high consumption of the reagent due to the potential chelation with other cations, such as Ca²⁺ and Fe³⁺, dissolved in the washing solution [64]. Competition in the metal–EDTA system is controlled by dissolved metal concentrations, reaction kinetics and certain soil parameters. Factors affecting the stability of metal chelate include: (1) the size and number of rings; (2) ligand substituents on the rings; (3) the nature of the metal; (4) pH of the washing solution; and (5) high content of calcite (CaCO₃) in the soil [75]. The concentration of Fe³⁺ in the washing solution is a crucial parameter for the stability of metal–EDTA complexes because Fe³⁺ may

Table 6
Examples of metal removal efficiency with EDTA according to the soil characteristics and metal fractionation

Leaching method (EDTA dosage)	Soil description	Soil characterization					Metal	Conc. ($\mu\text{g/g}$)	Metal fractionation ^a (%)					RE ^b (%)	Ref.
		Soil pH	CEC ^c (cmol/kg)	Sand/Silt/ClayOM ^d (%)	Ca (%)				F1	F2	F3	F4	F5		
Batch leaching 24 h 1 step, pH 4 (0.2 mol/L)	Soil from battery site, St-Jean-sur-Richelieu, Canada	7.6	–	–	0.7	6	Cd	27	10 ^e	26	23	22	20	<10	[54]
							Pb	24,600	2 ^e	47	43	5	2	98	
							Zn	241	2 ^e	12	48	21	17	58	
Batch leaching 30 min, 1 step (0.02 mol/L)	Soil from storage facility, Montreal, Canada	7.5	9 .5	52/33/16	12.5	–	Cd	56	<1	36	9	7	48	35	[76]
							Pb	17,944	<1	60	19	2	18	66	
							Zn	8940	<1	40	50	<1	9	42	
							Ni	364	4	8	21	8	59	15	
Heap leaching, 24 h, 4 steps (0.04 mol/kg)	Soil from mining site, Mezica Valley, Slovenia	7.1	23 .3	56/32/11	9.3	–	Pb	1243	<1 ^e	24	<1	56	8	80	[78]
							Zn	1190	<1 ^e	8	2	15	61	19	
Batch leaching, 30 min, 1 step, pH 7 (0.002 mol/L)	Artificially contaminated soil	4.7	52	42/33 ^f	2.4	0.1	Cd	269	80	7	11	2	0	>95	[73]
							Pb	2510	39	38	19	4	0	>95	
							Ni	605	23	7	4	61	4	40	
Batch leaching, 24 h, 1 step, pH 6 (1 mol/L)	Soil from smelter site, Palmerton, PA	–	–	–	–	–	Cd	280	26	12	22	38	2	53	[53]
							Pb	812	17	7	44	26	6	<10	
							Zn	2700	20	8	38	6	28	28	

^a F1 = exchangeable, F2 = acid soluble/carbonate bound, F3 = reducible/Fe–Mn oxides bound, F4 = oxidizable/organic matter bound, F5 = residual.

^b Removal efficiency.

^c Cation exchange capacity.

^d Organic matter content.

^e Water soluble + exchangeable fractions.

^f Sand/silt + clay.

form more stable complexes with EDTA ($\log K = 26.5$ at 25°C and ionic strength = 0.01) compared to the most heavy metals such as Cu ($\log K = 19.7$), Pb (19), Zn (17.5), Cd (17.4) [56,63]. The complexation interference of Ca^{2+} appears less problematic (thermodynamically) because Ca^{2+} forms much less stable complexes with EDTA ($\log K = 10.65$) than Cd, Cu, Pb, and Zn [63]. On the other hand, a recent study [64] showed that Ca^{2+} is the main competitive cation because CaCO_3 is strongly dissolved in the EDTA leaching solution at pH 4–5, thus concentrations of Ca^{2+} in the leaching solution is very high compared to the targeted heavy metal for the chelation with EDTA. Furthermore, complexation competition between heavy metals (such as Zn vs. Pb) may occur in leaching process [77].

Metal extraction also depends on the combination of many parameters such as EDTA/metal molar ratio, leaching method (batch vs. column/pile leaching), mode of reagent addition (single step vs. successive extraction steps with low reagent dosage), solution pH, liquid/solid ratio, and extraction time (Table 4). Multiple-step procedures with a low EDTA dosage gave best results compared to the single-step mode with a high dosage [78]. Leaching with EDTA is usually performed at pH 4–8 (Tables 4 and 6). At low pH values, the EDTA–metal complexes can be re-adsorbed on soil surface sites [74].

EDTA regeneration is a crucial parameter to the leaching process in order to avoid the release of EDTA into the environment. EDTA must be recycled in order to keep treatment costs at a reasonable level [76]. Several procedures have been proposed for EDTA regeneration (or degradation) and the removal of the metals from the leaching solution: (1) metal precipitation and EDTA regeneration via addition of the chemical agents; (2) electrochemical procedures; (3) ion exchange resin; (4) nano-filtration; (5) degradation of EDTA by oxidation and metal recovery by absorption (Table 4). For instance, Lim et al. [73] have proposed a protocol of regeneration and metal-precipitation using three steps: (1) metal substitution with Fe^{3+} to form $\text{Fe-EDTA} + \text{Me}^{2+}$; (2) metal precipitation with Na_2HPO_4 to form metal phosphate; and (3) Fe precipitation and EDTA regeneration with NaOH addition to form $\text{Na}_2\text{-EDTA} + \text{Fe}(\text{OH})_3$. With this process, the metal recovery was 85%, 89%, and 90% of the extracted Pb, Cd, and Ni, respectively. Reused EDTA was slightly less efficient compared to fresh EDTA in metal removal [73].

4.5. Surfactant-enhanced solubilization

Although the use of surfactants is more suitable for the treatment of organic contaminants, the removal of metals from soil by surfactants is also an interesting chemical procedure to be investigated. Recently, the use of surfactants has been studied to enhance the EDTA leaching process for metals mobilization from soils [76]. The surfactant addition in washing solution aims at assisting desorption or/and dispersion of contaminants from soils. When the metals are closely associated with organic contaminants, washing by surfactants can be more effective. Association between metal and soil substrates, and acidic or basic conditions are important parameters for soil washing success with surfactants. Mulligan et al. [79] indicate that a caustic surfactant could be used for removing the organically associated

metals while acidic surfactant could be employed for extracting the metals bound to carbonate and oxide. Several laboratory studies showed that cationic forms of metals can be extracted from contaminated soils and sediments by anionic biosurfactant solutions [80–83]. However, the metal extraction by biosurfactants has not yet been performed for large-scale remediation projects [84].

4.6. Reducing and oxidizing agents

Reducing and oxidizing agents provide yet another option to enhance solubilization of metals since chemical oxidation/reduction can convert metals to more soluble forms. USBOM and USEPA have conducted laboratory research on Pb extraction involving redox manipulations and valence changes to promote solubilization and recovery of various Pb compounds from synthetic contaminated soils [75]. Some laboratory studies showed that the addition of reducing agents can enhance metal mobilization by EDTA [11,51,52]. The use of reducing agents contributes to the dissolution of Fe–Mn oxides, thus enhancing metal removal bound to Fe–Mn fraction in the EDTA leaching process [51].

Several oxidant agents are also used to enhance the removal of metals. Lahoda and Grant [85] proposed the use of an oxidizing agent to enhance the solubilization of metals from fine particles into a soil washing process comprising particle separation, metal solubilization, and metal precipitation. Lin et al. [70] used sodium hypochlorite (NaClO) as an oxidizer agent in the chloride-based leaching process (2 M NaCl at pH 2) to extract metallic Pb-particles (smaller than 0.15 mm) and other Pb-species from highly contaminated soils (washing results are reported in Table 1, projects #29 and 30). Reddy and Chinthamreddy [86] reported that complete removal of Cr from clayey soils (artificially contaminated) was achieved with the leaching process using a 0.1 M potassium permanganate (KMnO_4) solution.

4.7. Integrated process train of chemical extraction

On large-scale operations, leaching methods are classified into two main classes: (1) percolation leaching such as heap/pile leaching or vat leaching; (2) agitated leaching based on batch step or continuous procedure [49]. In the heap leaching process, soil is piled in a heap and the leach solution is sprayed over the top of the heap, and allowed to percolate downward through the heap [49]. The agitated leaching method is performed under turbulent flow conditions. For soil treatment at commercial-scale, heap/pile leaching appears more cost effective [61,63,78]; however the extraction processes can be slow and metal concentrations must be relatively high. Agitation leaching is an interesting method for soil treatment because it can allow aggressive and effective extraction of the metal contaminants from soils [44]. The column washing tests resulted better metal removal efficiency rather than batch tests [11,78]. Abumaizar and Smith [11] reported that the continuous flow in the column promoted the flushing of the reaction reagent/metal complex and minimized the re-adsorption of complex on the soil surface.

After dissolution of the metal compounds, it is necessary to separate the leaching solution from the residual solid phase of soil. The resulting solution containing metals can be treated by various aqueous processes such as precipitation, sedimentation, complexation, electrochemical techniques, liquid ion exchange, resin ion exchange, or membrane technologies to recover metals (Table 4). Solvent extraction techniques make it possible to selectively transfer certain ionic metal species present in an aqueous washing solution to an organic liquid phase if the extracted metal compounds are preferentially soluble in the organic phase [49]. The washed soil is usually rinsed with water to remove the residual extracting agents from the soil. Depending on the soil characteristics and reagents used, the resulting 'clean' soil fraction can be returned to the site or must be disposed off-site.

4.8. Advantages/disadvantages of chemical extraction technologies

The advantages/disadvantages significantly diverge according to the reagents and extraction method used. Specific comments were discussed in the preceding sections. Generally, the principals advantages of chemical procedures compared to physical separation are: (1) the sorbed metal forms can be treated; (2) certain metal compounds can be dissolved; (3) the fine-grained soils may be treated in certain cases; (4) the extracted metals may be easily recovered by a wide variety of methods. Chemically enhanced soil washing can become attractive if the chemical reagents are recycled, detoxified or not hazardous.

The large-scale application of chemical extraction processes presents numerous disadvantages: (1) the use of chemical agents significantly increase processing costs; (2) the processed soil may be inappropriate for revegetation and on-site disposal because the physico-chemical and microbiological properties have been affected; (3) the presence of toxic chemical agents in the final soil or the residual sludge may be problematic for disposal; (4) the presence of certain chemical agents in the wash fluid can complicate water recycling and treatment, thus increasing cost of the overall process; and (5) the treatment of sludges rich in metal can be difficult. The chemical agents involved may cause other environmental problems. For instance, the soil treated by EDTA leaching may potentially be hazardous to reuse if a part of the chelating agent remains in the soil. Wastewater treatment may produce large amounts of toxic sludges that must be carefully managed.

5. Combination of physical separation and chemical extraction

Table 1 reports 18 processes combining physical and chemical procedures. The complementary use of the physical particle separation and chemical leaching procedures provides a very useful tool for decontaminating the soils affected with metals. The typical combination uses physical separation (primarily by size, density or floatability properties) to concentrate particulate forms of metals into a small volume of soil, followed by chemi-

cal extraction of this concentrated fraction to dissolve the metals (Table 1, projects #17–27, 29, 30, and 33). For example, a combination of the BESCORP physical separation technology and the COGNIS-Terramet Pb extraction process has been efficient at Superfund site in New Brighton, MN (Table 1, project #20). In this case, the sand fraction is treated by density separation (jig), while fine fractions are treated by chemical leaching. The Pb removal efficiency for the fine fractions ranged from 65% to 77%. Lead concentrates were delivered to a Pb smelting facility.

Many soil washing processes are based on simple particle size separation using hydroclassification and attrition scrubbing with water-based fluid. Particle size separation is often used before chemical extraction, with the assumption that the fines contain most of the metal contamination. Since metal concentrations are usually high in the fine fraction, the practice of direct disposal is inappropriate. Chemical extraction may be used for the decontamination of the fine fractions and can allow metals recovery in a saleable form or concentrated form.

Soil washing systems may involve other combination types depending on the soil matrix characteristics, metal speciation and type of metal to be treated. The combination of PS/CE can be reversed (e.g., chemical leaching followed by wet screening) or may involve a simultaneous process of PS/CE methods. For instance, certain processes use attrition scrubbing chemically enhanced with acids, surfactants or chelating agents followed by a wet screening/hydrocycloning stage to separate the fine particles/washing solution (containing the pollutants) from the clean fraction (Table 1, projects #28, 31, and 32). The grinding and crushing process of soil particles may be a pre-treatment option for enhancing the efficiency of the chemical extraction treatment. The use of ultrasounds may accelerate the surface cleaning of soil particle and improve the leaching of metals [87–89]. The influence of ultrasounds contributes through several mechanisms (not fully understood) such as the micro-fragmentation of particles, and disturbance of solid/liquid interface by cavitation [87].

The soil washing treatments aim at completely decontaminating the site by removing metals from the soil matrix. Table 1 reports the treatment efficiency for total metal concentrations. However, the aspect of reduction in metal leachability to below standard TCLP is also important in the quality results of soil washing. The ideal goal of an extraction strategy is to recover metals for reuse and resale, however, metal recovery is often not practicable for projects that lack economic viability or technical feasibility for the extraction and recovery processes. The generated toxic sludges (containing metals), which are recalcitrant to a metal recovery treatment, may require a stabilization/solidification process prior to disposal. In many cases, soil washing is used to reduce the metal concentrations to an acceptable level or to considerably reduce the volume of contaminated soil.

6. Status of soil washing technology

This section provides a discussion about the use, at large scale, of soil washing for the remediation of sites polluted by metals. The discussion focuses on the status of soil washing

systems employed in the US, Europe, and Canada (Table 1). Soil washing based on physical separation (SW–PS) is more employed than processes that use chemical extraction (SW–CE). Chemical extraction is more expensive (\$ 358–1717 m⁻³) compared to physical separation (\$ 70–187 m⁻³) [4].

6.1. Soil washing in Europe

SW–PS is relatively well established in Northern Europe, primarily in the Netherlands since the mid 1980s [4,90]. The Netherlands are a pioneering country for the implementation of the SW–PS technology in a soil remediation context. For instance, Heidemij (now ARCADIS), has used a SW–PS technology since 1983 [91]. Soil washing systems used in the Netherlands is particularly appropriate to treat metal contaminants and typically involve attrition scrubbing, hydrocyclones, upstream columns, spirals and froth flotation cells [90]. A literature review revealed that many Dutch environmental companies offer soil washing system such as: ARCADIS (<http://www.arcadis-global.com>); A&G Milieutechniek (<http://www.aengbedrijven.nl>); Boskalis Dolman (<http://www.boskalisdolman.nl>) [5]. In 2001, 21 stationary and four mobile soil washing plants were operational; and 855 kt/year were treated between 1991 and 2001 [90]. Environmental Dutch firms have introduced and promoted the development of SW–PS in the United States in the early 1990s and in Japan in the early 2000s [92,93].

The SW–PS technology is also well established in Germany, Sweden, Norway, and Belgium [5,7,19,91] to treat metal-contaminated soils. Ten Swedish companies and three Norwegian companies offer treatment by soil washing applicable to metal-contaminated soils [5]. Metso, a Swedish based company, has been a major supplier of physical separation technologies for European soil washing processes since the 1980s [34]. Metso was the equipments supplier for the first US project of soil washing, conducted by ART [34].

6.2. Soil washing in the USA

Griffiths [7] reported two soil washing systems developed by USEPA in the 1980s: the mobile soil washing system (MSWS) based on chemical extraction, and the volume reduction unit (VRU) based on size separation. According to USEPA [8], the significant applications of SW–PS for remediation of metal-contaminated soils in the United States began in the early 1990s and the first applications were focused on treating Pb-contaminated soils of abandoned small arms firing ranges (SAFR). For instance, in 1991 US Bureau of Mines presented a conceptual physical separation process train for the remediation of SAFR, which included Pb recovery [9,94]. Since the mid 1990s, Brice Environmental Services Corporation (BESCORP) has had extensive experience for SAFR remediation (Pb removal by density separation) and has also applied physical separation for the remediation of a battery-manufacturing site in 1995 (Table 1). Soil washing systems have also been used since the early 1990s for treatment of soils from wood preserving sites contaminated by a mixture of metals (Cu, Cr, and As) and organic

contaminants [8]. For example, the BioTrol Soil Washing System has been employed at the MacGillis and Gibbs Company site in New Brighton, MN in 1992 [95]. In the mid 1990s, the US Army Corps of Engineers (USACE) and the USEPA reviewed physical separation technologies and concluded that these techniques, coupled with chemical extraction, offered the most promising method for metal remediation in soils [9].

The co-operation with Dutch environmental firms has contributed to the establishment and the development of soil washing in the United States [92,96]. In the early 1990s, the firms Geraghty & Miller Inc., USA and Heidemij Realisatie of The Netherlands formed a joint venture (now called ARCADIS) and were incorporated as Alternative Remedial Technologies (ART) to introduce the Heidemij soil washing system to the US market [92]. The first project contracted under this arrangement was the large-scale remediation of the King of Prussia Superfund site, NJ performed in 1993 [6].

The number of soil washing technologies available at commercial-scale for the treatment of metals in the US is difficult to estimate. ITRC [20] compiles a list of 16 soil washing technologies available in the US for full-scale applications. The REACH-IT database [97], which compiles 500 remediation technologies, reports only seven vendors of soil washing technology and one vendor of an acid extraction process. On the other hand, FTRT [98] compiles 20 vendors of soil washing or acid extraction technologies. The main US vendors of soil washing technologies, presented in Table 1 are: BESCORP; ART Engineering LLC; Eddy and Metcalf; and Biogenesis. Various soil washing systems have been tested to remove metals from soils in the framework of Superfund Innovative Technology Evaluation (SITE) demonstration program (Table 1).

Although the soil washing technology is available at commercial-scale in the US, its use has been limited for remediation of Superfund sites when compared to the conventional solidification/stabilization technology. The Annual Status Reports (ASR) database [99] indicates that the soil washing method has been implemented at only two Superfund sites contaminated with metals: at King of Prussia, NJ (completed) and at Vineland Chemical Co., NJ (in operation) (Table 1). Table 7 reports several cases of soil washing projects that have failed in the framework of the Superfund program and give the principal reasons for soil washing failure in the remediation of metals.

6.3. Soil washing in Canada

Table 1 reports some examples of soil washing systems performed at pilot-scale or full-scale in Canada such as: (1) Tallon Metal Technology in Montreal and Toronto; (2) Toronto Harbour Commissioner (THC) treatment train in Toronto; (3) pilot demonstration by Alex-Sol and INRS; and (4) pilot demonstration by Dragage Verreault and INRS. Holbein [100] reported on the soil washing process of Tallon Metal Technology (Guelph, Ontario) for mixed contaminants; the soil treatment involved physical separation to treat the coarse fraction, and a chemical process to treat the fines. Three large-scale applications of Tallon's treatment system have been applied. Researchers from

Table 7
Examples of deselected soil washing projects in Superfund program

Site location and description	Media	Metals	Reasons of soil washing failure	Alternative selected technology
Sacramento Army Depot, oxidation lagoons, OU4, CA	Soil	Cr, Pb	Costs	Solidification/stabilization; Off-site disposal
Zanesville Well Field, OH	Soil	As, Cr, Hg, Pb	Soil volume was much smaller than originally projected; determined to be too expensive	Off-site disposal
Ewan Property, OU 2, NJ (industrial waste dumping)	Soil	Cr, Cu, Pb	Soil volume was much smaller than originally projected	Off-site disposal
Gould Inc., Portland, OR (battery site)	Soil	Pb	Soil washing was shown to be ineffective due to varying site conditions	Capping the landfill
United Scrap Lead/SIA, OH (lead battery recycling)	Soil/sediments	As, Pb	Costs	Soil disposed off-site if Pb levels above 1550 µg/g; containment of soil below this level
Myers Property, NJ (pesticide manufacturing)	Soil/sediments	Cu, Cd, Pb, As	Soil washing treatment was not successful for As during treatability study	Off-site disposal

Data extracted from [124,125].

INRS ETE (University of Quebec) have tested several pilot-scale soil washing systems for the decontamination of brownfield soils located in urban environment [22,101,102].

7. Conclusions

Soil washing is a technology particularly relevant for the remediation of metal-contaminated soils. The majority of projects are based on physical separation technologies which are cost effective and well established in the mineral processing industry. From the economic and environmental point of view, soil washing may be an effective alternative to solidification/stabilization and landfilling. The soil washing technology presents many advantages: (1) the processes attempt to permanently remove metals from soils and can allow recycling of metal in certain cases; (2) the volume of contaminated soil is markedly reduced; (3) the processed soil can be returned to the site; and (4) the process duration is typically short to medium-term compared to other metal extraction methods. However, the success of the soil washing process requires: (1) an exhaustive soil characterization; (2) a study of metal speciation and fractionation; and (3) an understanding of the relationship between the soil matrix and metals. The complementary use of the sequential extraction procedure and the SEM–EDX provides a very useful analytical tool for understanding chemistry aspects of metals in soils and predicting the soil washing treatment efficiency.

Soil washing can be used independently or in conjunction with other treatment technologies. While frequently used in Europe, the soil washing method has not been used extensively in the US and in Canada. Soil washing has been performed successfully in Europe, due in part to regulatory actions taken to drastically restrict landfilling options. The soil washing technology is often used for reducing the volume of soils and residues placed in landfills. Soil washing in Europe is mostly performed in fixed facilities, while mobile soil washing plant appears to be more common in the US and Canada.

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